

**CASE FILE
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**DEVELOPMENT OF SPACE STABLE, LOW
SOLAR ABSORPTANCE, PIGMENTED
THERMAL CONTROL COATINGS**

**National Aeronautics & Space Administration
Langley Research Center
Langley Station
Hampton, Virginia**

IIT RESEARCH INSTITUTE

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(Final Report)

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DEVELOPMENT OF SPACE STABLE, LOW SOLAR ABSORPTANCE,
PIGMENTED THERMAL CONTROL COATINGS

October 17, 1968 to October 16, 1969

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FOREWORD

This is Report No. IITRI-C6166-12 (Final Report) on IITRI Project C6166, Contract No. NAS1-8166, entitled "Development of Space Stable, Low Solar Absorptance, Pigmented Thermal-Control Coatings." This report covers the period from October 17, 1968 through October 16, 1969.

Major contributors to this program include John E. Gilligan, Project Leader, John Brzuskiwicz, and Gene A. Zerlaut. Other contributors include S. Shelfo, sample preparation; M. Jackson, fine particle analyses and consultation; G. Yamate, electron microscope and particle geometry analyses; Dr. O. Johari and Miss I. Corvin, Scanning Electron Microscope; B. Boldt, DTA/TGA analysis; and G. Kimura and L. Gillilan, irradiation and gas adsorbate tests and measurements.

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Respectfully submitted,
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ABSTRACT

This research program has been conducted to provide an overall analysis and evaluation of the technical considerations involved in pigmented, low solar absorptance coatings. Initially, a theoretical effort was conducted, directed toward the development of a comprehensive model relating spectral reflectance to the the fundamental properties of materials and to the changes induced in them by the space environment. The majority of the effort was experimental, involving mainly light scattering experiments, because, the theoretical efforts indicated that multiple scattering and the effect of particle size were the least understood of the several important factors in the models.

Reflectance of white pigmented coatings and the environment-induced response of the fundamental properties determining it was formulated in terms of three models. The first defines spectral reflectance in terms of gross parameters (PVC, particle size, etc.) and the indices of refraction and absorption of the components.

The second model attempts to relate the changes in the gross spectral absorption coefficient as a function of the interaction of ultraviolet radiation and charged particles with fundamental materials properties. In the third model, the relationship between these changes and the gross spectral reflectance is stated in general terms.

In the experimental program spectral reflectance was measured against the parameters of discrete particle size, aggregate size, film thickness and film structure. The powders were characterized by several techniques including BET, and optical and electron microscopy. Scanning electron microscopy was used to study and characterize binderless films. The effects of film structure, which depends in part upon the nature of the materials, the preparation methods and application techniques, were especially noted. This structure, consisting of the discrete particles, their aggregates and the void spaces in and between particles and aggregates, strongly influences spectral reflectance.

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DEVELOPMENT OF SPACE STABLE, LOW SOLAR ABSORPTANCE,
PIGMENTED THERMAL CONTROL COATINGS

I. INTRODUCTION

Historically, the major task in developing low solar absorptance, pigmented, thermal control coatings ("white paints" for spacecraft temperature control) has been in making them resistant to the effects of the hostile elements of the space environment, notably ultraviolet (UV) radiation and charged particles. In the last few years the approach to developing stable coatings involved fundamental studies of mechanisms of degradation. IITRI's approach (Ref.'s 1, 2), for example, in other programs has been to elucidate mechanisms of ultraviolet degradation in specific materials and then to devise protective schemes. This has been accomplished successfully with both zinc oxide and zinc orthotitanate, both large band gap semiconductor pigments. These pigments have an ultimate α_s limit of the order of 0.13 - 0.15. To achieve lower α_s paints, larger band gap materials are needed. Two major problems, however, become evident, one relating to intrinsic absorption processes, and the other to the vehicle.

In semiconductor materials, fundamental absorption is usually so strong that interactions with ultraviolet are usually at or very near the surface; in dielectric materials with larger band gaps the fundamental absorption coefficients are considerably less and the ultraviolet interactions occur much more frequently within the bulk. The net effect of a reduced absorption coefficient then is to make ultraviolet interactions more evenly distributed within the pigment particles and hence to maximize impurity or defect related interactions. The other problem is that when the band gap is increased, the pigment obviously becomes more transparent in regions in which the vehicle absorbs ultraviolet

radiation. Thus, the wider the region of transparency, the greater is the probability of incurring ultraviolet damage in the vehicle.

In this program, we have considered the broadest aspects of reflectance and reflectance stability. A key area of investigation was the role of pigment particle size in determining spectral reflectance and in its effect upon reflectance stability. It was evident at the outset that, of the many parameters controlling or affecting reflectance, the basic processes of light scattering were the least understood - both basically and in terms of their role in real paint systems. The initial efforts consequently were devoted to the development of mathematical models relating reflectance to the extrinsic (environmental) and intrinsic (materials-related) parameters. These models will be examined and discussed in detail. The theoretical effort was accomplished essentially independently of the experimental work, primarily because the theoretical effort was very small compared to the experimental work - which was almost entirely light scattering.

The materials selected for this study were logical choices for low absorptance pigments; they possessed high transparency to ultraviolet and visible radiation, and, above all, had with one exception an extensive and thorough literature background. Alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2) and lanthana (La_2O_3) were the original choices; the main reason for the choice of lanthana was its excellent resistance to the effects of proton (solar wind) damage, even though it has poor stability in ultraviolet.

The context of the experimental work was in relation to the theoretical models: the role of light scattering in the overall model. A main objective was to determine whether the parameters that intensify spectral reflectance also intensify the absorption effect of an induced color center. By appropriate choice of parameters the reflectance of a paint system may be increased in

selected spectral regions, but it is of major importance to understand the effects on other desired properties of the paint system, especially its environmental stability. Thus we have held to the philosophy that, while it is important to understand the role of each major parameter, it is also important to understand the relationships between them.

This report is divided into two major categories - one, dealing with our theoretical and analytical model efforts, and the other, with the experimental work (almost entirely light scattering). The first section of the report describes the theoretical development; the second part involves mainly the experimental work - in which we also make some comments about the meaning of the experimental data. The results and a discussion of them and the conclusions are given in the last two sections.

Certain commercially available materials and test apparatus are identified in this report to adequately specify the materials and apparatus employed. In no case does this identification constitute an endorsement of these products by the National Aeronautics and Space Administration or the IIT Research Institute.

II. THEORETICAL MODELS

A. Basic Requirements

In a broad sense the ultimate objective of this program is to develop a general model for space-induced changes in solar absorptance of thermal radiative coatings, a model which accounts for reflectance in terms of both elementary and macroscopic properties of materials. Such a model, from a theoretical point of view, should relate gross spectral reflectance to at least those characteristic parameters or materials' properties to which it is most sensitive.

To identify the parameters of greatest significance in the selection of stable materials for spacecraft thermal control essentially requires the following: an empirical knowledge of the important parameters defining and/or controlling the spectral reflectance properties of a pigment-vehicle system and a fundamental understanding of why such parameters are important; a knowledge of the physical and chemical changes in the components of a paint system during exposure to the space environment and also of the rates at which such changes occur; and finally, an appreciation for the effect these changes have on the spectral reflectance properties of the paint system as a whole.

B. The General Degradation Model in Outline

The general model, as we envision it, consists of three inter-related specific models. The first is one which determines the spectral reflectance properties of a dispersed pigment vehicle system by relating measurable macroscopic parameters to basic materials properties. The second calculates the damage induced by the space environment; in this case mechanisms specific to the individual components of the paint system and the damage kinetics (which are determined by both environment parameters and materials properties) are specified and related. This model therefore predicts the rates of accumulation of all environment-induced defects which are significant in terms of solar absorptance, α_s . The

third model estimates the changes in spectral reflectance which result from the additional absorption, that is, due to the combined effect of the individual induced defects.

An approach to the first model would at first deal with particle size versus wavelength as an important index of the amount of scattering a particle contributes to a system of dispersed particles. Theoretically, and actually, the ratio of index of refraction between a pigment and its environs is also very important. The mathematical form of such a model, however, will be dealt with in the section on light scattering. In the following we will confine our discussions to the mathematical development of an induced defect model.

C. Mathematical Development

We will first set the basis for the second and third models and will attempt to explain each of the terms in the mathematical development. In the following is a brief sketch of the theory of induced absorption and a relationship between the induced absorption index and the number density of defects causing it.

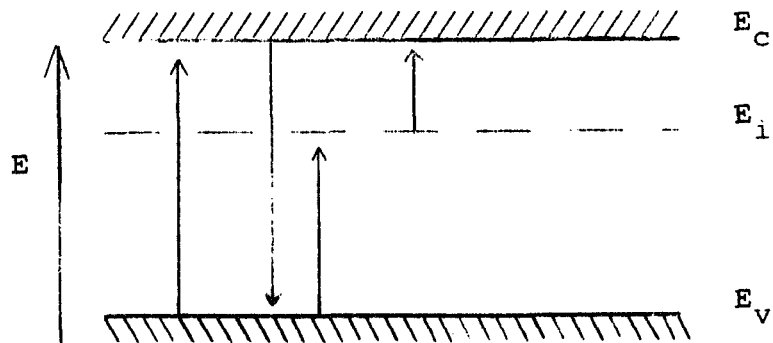


Figure 1. SCHEMATIC ENERGY LEVEL DIAGRAM

Consider Figure 1, where we have drawn the electronic energy level diagram of a dielectric material. The uppermost level is the conduction band; the lowermost, the valence band. With no impurities or electronic defects present in the lattice, the only allowed transition for an electron in the valence band is to the conduction band.

Now, if a defect is generated in the crystal, the electronic distortion in the vicinity of that defect effectively introduces new levels locally into the crystal. For example, if a single valence anion is removed from its normal lattice site and is replaced by an electron, the electrical neutrality of the crystal at that site is not altered; but the charge distribution and thus the local electronic energy levels are changed. This new level is represented in Figure 1 by the broken line, and designated E_i . The arrows indicate the electronic transitions possible, and it is evident that the creation of one defect introduces two absorption bands not otherwise present in the host lattice, one band corresponding to the transition from the valence band to the defect level ($E_v \text{ --- } E_i$); the other from the defect level to the conduction band ($E_i \text{ --- } E_c$).

Two important aspects of these induced absorptions are their probability of occurrence and their spectral character. The probability of occurrence depends upon population density, i.e., the number density of the electrons in each of the two levels between which the transition occurs. The spectral character of the induced absorption depends upon the distribution of energy sub-levels within each level; a wide band will result if there is a large energy spread in both levels; a narrow one if the energy spread in either band is small. Dexter (Ref. 3) using quantum mechanical concepts, has performed a theoretical analysis of the intensity and shape of an induced absorption band. Except for the interpretation of certain terms, Dexter obtains the same result as is reached in classical analyses. The mathematical

result is expressed in Eq. 1 (see Section IV for a complete development of this relationship).

$$\epsilon = (n - ik)^2 = \frac{4\pi N_i e^2 f_i}{m_i} \cdot \frac{\omega_{o,i} - \omega}{(\omega_{o,i}^2 - \omega^2) + i\omega g_i} \quad (1)$$

After multiplying Eq. 1 by the complex conjugate and separating it into real and imaginary components, we have

$$n^2 - k^2 = \frac{4\pi N_i e^2 f_i}{m_i} \cdot \frac{(\omega_{o,i}^2 - \omega^2)}{(\omega_{o,i}^2 - \omega^2)^2 + \omega^2 g_i^2} \quad (2a)$$

$$2nk = \frac{4\pi N_i e^2 f_i}{m_i} \cdot \frac{\omega g_i}{(\omega_{o,i}^2 - \omega^2)^2 + \omega^2 g_i^2} \quad (2b)$$

The notation is as follows:

- n , the index of refraction (dimensionless)
- k , (induced) extinction coefficient (dimensionless)
- N , the number density of induced defects, defects/cm³
- e , the electronic charge (esu units)
- f , the oscillator strength (dimensionless)
- m , the electronic mass (effective), grams
- ω , the frequency ($= 2\pi \cdot c/\lambda$), radians/sec
- $\omega_{o,i}$, the peak absorption frequency, (corresponds e.g., to $E_i \longrightarrow E_c$)
- g , the damping factor, radians/sec.
- i , a subscript indexing the i^{th} type defect.

The term $2nk\omega$ has its peak value at $\omega = \omega_o$, and half this value occurs at a $2nk$ value of $\pm g/2$ on either side of ω_o . The damping factor g , therefore, is a measure of the breadth of the levels involved in the transition, while ω_o indicates their nominal energy separation. At any given wavelength the induced absorption will be dependent linearly upon N_i . In practice it is common to deduce N_i from the induced absorption through the Smakula relationship (Ref. 4)

$$N_i f_i = \frac{8.21 \times 10^{16} n W_i}{(n^2 + 2)^2} \quad (3)$$

in which W_i is the area under the absorption curve due to i^{th} type defects, $\text{eV} - \text{cm}^{-1}$. Equation 2b describes the theoretical shape of an induced optical absorption band, and it is observed in many materials; a gaussian shape however, occurs somewhat more frequently. The gaussian curve is analytically expressed as

$$2nk = \frac{4\pi N_i e^2 f_i}{m_i} \cdot \exp \left(- \frac{(\omega - \omega_{o,i})^2}{(4 \cdot \ln 2) g_i^2} \right) \quad (4)$$

Band shapes which are nearly parabolic, and some which are not even symmetrical are not unusual.

In essence we will be concerned less with actual bandshape than with the parameters which characterize it and their significance. Consider, first, the bandshape shown in Figure 2 in which α_{max} is the peak absorption (dimensionless), ω_o the frequency (or energy) of the peak, and g the width of the peak in frequency (or energy) units at the half-height of the curve.

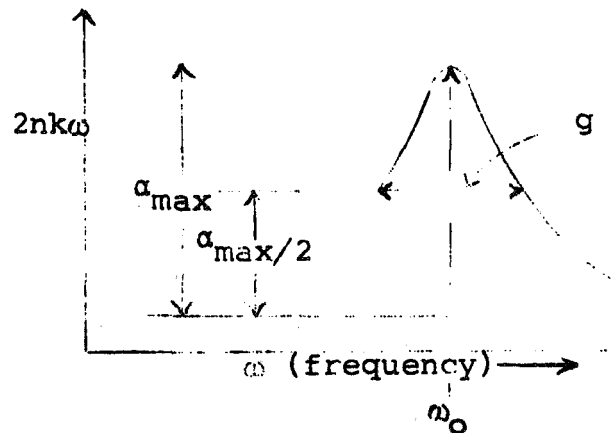


Figure 2. ABSORPTION SPECTRUM OF AN INDUCED DEFECT

The significant points we wish to develop regarding Eq.'s 2a and 2b are these.

First, these equations pertain to transmitting, non-scattering systems, hence their utility in scattering systems must be established. Second, it seems necessary to show how the theory involved can be tested experimentally, or, conversely, to show how experimental reflectance degradation results can be interpreted in theoretical terms. Third, the numerical values of ω_o , g , and f must be elicited for each defect; and, for materials in which the induced bands overlap strongly, this may be a formidable task. These, however, are intensive properties; consequently $2nk$ is related directly to the number concentration of defects which is the only time dependent variable in Eq.'s 2a and 2b.

Note that Eq.'s 2a and 2b may be written

$$2nk = N_i(t) \cdot A_i \cdot F_i(\omega_o, g), \quad (5)$$

where

$$A_i = e^2 f_i / 4\pi m_i$$

$$F_i(\omega_o, g) = \frac{\omega g_i}{(\omega_{o,i}^2 - \omega^2)^2 + \omega^2 g_i^2} \text{ (or other band shape)}$$

The term $F_i(\omega_o, g)$ is the mathematical description of the band shape. In practice what is measured in non-scattering systems is the extinction, $\exp(-K_a x)$, where

$$K_a = 4\pi k_a / \lambda$$

A scattering system likewise has attenuation which may vary with wavelength. We assume that scattering and absorption are independent processes. The total attenuation due to scattering and true absorption is then

$$R = R_o \exp(-(K_a + K_s)x) \quad (6)$$

Equation 6 now becomes a definition of reflectance in the sense that, when K_a (which is a function also of $N_i(t)$) is zero, $R = R_o e^{K_s x}$, and when x increases, reflectance increases. Implicit

in this definition is the assumption that the color centers responsible for K_a do not also significantly alter K_s . This assumption, of course, must be tested, but it seems likely that, if index of refraction is the major intrinsic parameter in scattering, the change in n and hence in scattering, will be negligible. An analogous assumption that the total true absorption is not influenced by scattering seems patently invalid.

Rewriting Eq. 6, but retaining the notion that there may be some interaction between K_s and K_a through N_i we have

$$R = R_0 \exp(-c_s K_a x) \cdot \exp(K_s x) = R_0 \exp(-4\pi c_s k_a x) \cdot \exp(K_s x) \quad (7)$$

Where c_s is the spectral scattering cross-section which in this case is the ratio of the true absorption in a scattering system to that in an equivalent non-scattering system.

Combining Eq. 5 and 7 gives

$$R = R_0 \exp - \left[2\pi c_s (A_i F_i N_i(t)/n_i) x \right] \exp(K_s x) \quad (8)$$

Equation 8, it must be remembered, gives the spectral value of the reflectance for a material with one type of defect contributing absorption; for several types of defects, their effects at a given wavelength must be summed:

$$R = R_0 \exp - \left[2\pi c_s \sum_i (A_i F_i N_i(t)/n_i) x \right] \exp(K_s x) \quad (9)$$

There are several deductions we can make at this point. First, it is obvious that the reflectance decreases exponentially with defect concentration. This behavior is well known and documented. Secondly, we begin to see the importance of the index of refraction. Since the scatter cross-section c_s is a function of particle size (i.e., $d_p/n\lambda$), the importance of the index of refraction is made more clear by its appearance in the argument of the exponential.

The most important objective in the development of this general model is the identification of the important and relevant fundamental properties of materials, those solid-state properties which determine or influence their optical characteristics. For example, in the term $A_1 (= e^2 f_1 / 4\pi m_1)$, while the electronic charge, e , is a fundamental quantity, the effective electron (or hole) mass, m_1 , and the oscillator strength, f_1 , depend upon the local electronic structure, the wave functions of ground and excited states, and upon the relative energy separations of these states. So also does the $F_1(\omega_0, g_1)$ term; ω_0 and g are determined by energy level separation and by electron distributions within levels, respectively. The index of refraction arises mainly from the motion of electrons which respond to an externally applied electromagnetic field; it depends upon how many electrons per unit volume become "polarized" in the presence of an electromagnetic field.

The essence of Eq. 8 is not so much to establish a correct mathematical relationship for spectral reflectance or reflectance degradation; rather it is to act as a starting point for identifying those basic properties of materials which determine their reflectance characteristics. The rationale for a general model consisting of three "sub-models" is inherent in the basic mathematical arguments of Eq. 8 (or 9). The environment/materials interaction (induced defect) model is embodied in the relationship $N_1 = N_1(t)$; it depends upon both the environment parameters and basic materials properties. The terms A_1 and F_1 derive from basic materials properties only, i.e., the molecular electronic structure; they describe quantitatively and qualitatively, respectively, the induced absorption caused by the N_1 defects. The third model, reflectance/scattering, is essentially the term $(c_s/n_1)e^{K_s x}$, where c_s modifies the effect of the induced absorption on reflectance. It is seen from Eq. 8 that the higher the index of refraction the less the effect of an induced defect, but c_s is also an implicit function of the refractive index, n_1 . Actually, it is c_s which is the prime parameter of interest in Eq. 8. The term c_s in

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turn, depends not only upon fundamental atomic and molecular electronic structure which give rise to the refractive index, but also upon such microscopic properties of materials as crystal structure, crystallite size and shape, and such macroscopic properties as particle size and shape, particle density and bulk density.

D. Major Parameters in the General Model

Let us examine the above statements in concise mathematical notation: letting $E(r)$ be the electronic distribution of states in a molecule of a dielectric material, we can rewrite the terms of Eq. 8:

$$R = R_0 \exp - \left[2\pi c_s A_i F_i N_i / n_i \right] e^{K_s x} \quad (8)$$

in functional notation:

$$R_0 = R_0 \left[c_s (d_p, d_v, \lambda, n_i, \psi), \ell, E(r) \right] e^{K_s x} \quad (10a)$$

$$A_i = A_i \left[E_a(r) \right] \quad (10b)$$

$$F_i = F_i \left[E_F(r) \right] \quad (10c)$$

$$n_i = n_i \left[E_n(r), N_n(r), \lambda, a_k, r_k \right] \quad (10d)$$

$$N_i = N_i \left[\Phi_{i,j}, \lambda_{c,i,j}, \ell, t, T \right] \quad (10e)$$

where

- d_p = average particle diameter
- d_v = mean particle separation distance
- λ = wavelength
- ψ = particle shape factor
- N_n = density of polarizable electrons at wavelength λ
- a_k = molecular bond lengths
- r_k = crystal dimensions (atomic spacing/arrangement)
- $\Phi_{i,j}$ = fluxes of j type environments or processes capable of producing i^{th} type defects

$\lambda_{c,i,j}$ = equivalent longest wavelengths (minimum energies)
of the i th type environments/processes to cause i th
type defects
 λ = film thickness
 t = time
 T = temperature.

The significance of the $E(r)$ subscripts in the terms in Eq. 10b, 10c, and 10d is that the A_i , F_i , and n_i all depend upon the distributions of electronic levels and states, but each in a different way. For instance, it is known that the optical absorption caused by interactions with the external environment results from the introduction of new electronic energy levels in the band gap of a material; the index of refraction, however, is not altered significantly because the number density of polarizable (valence) electrons remains constant. We would like to write the explicit functionality for each of the relationships in Eq. 10, but this would be an enormous task. Rather, if we can point to certain fundamental properties common to at least two sub-models, we will have laid the ground work for understanding the degradation of highly scattering systems.

At this point in the development of the general model, we believe it is necessary to point out some of the conclusions we have reached in researching and developing the theories. First, there is no development of scattering theory outside of classical electromagnetic theory; modern quantum mechanics and solid state theory, to our knowledge, have not been applied to the problem of light scattering. Secondly, the concept of an index of refraction seems not to be understood in other than classical electromagnetic theory. We feel that this is a most serious hindrance to the understanding of light scattering, because it is obvious that index of refraction plays a major role in it. Thirdly, there appear to be no serious attempts made to correlate index of refraction with molecular and/or crystalline structures; i.e., structure-properties data do not exist in this area.

E. Optical Stability Criteria

1. General Requirements

In this document we will examine some fundamental concepts regarding the stability of materials and will attempt to place them in a context applicable to this program. Mainly we would like to know which fundamental properties of a material determine its initial optical properties, which determine the stability of these properties, and those which affect both. From experience we know that the stability problem exists mainly in white paint coatings. That ultraviolet and charged particle radiations can alter the optical properties of a space coating is, of course, very widely known. The choice of materials that can withstand the rigorous ultraviolet and charged particle environment of space, however, remains a serious problem. What we would like most to know are the criteria for selecting space stable materials.

2. Physical Requirements

We shall restrict our discussions to solid, dielectric, white (transparent, non-absorbing) pigments, even though we recognize that polymeric and other binder materials also degrade in the space environment. The basic requirements of a white paint are such that it must have very high diffuse reflectance throughout all or most of the solar spectrum. The pigment therefore must be transparent, and it must be a powder whose particles are of a size comparable to solar spectrum wavelengths, in order to promote multiple scattering. Such materials appear white to the eye. Since there are many such materials, we must apply further criteria to their selection, for example, high melting point, high index of refraction, insolubility in vehicles, etc. It is obviously not too difficult to determine and apply such criteria as these, and it is important from a practical viewpoint to do so.

3. Solid State Considerations of Stability

Our chief concern, however, is with more fundamental criteria--the criteria for selecting stable pigments. Such criteria obviously must also be consistent with the physical requirements outlined above. Perhaps the best approach is that of using the band theory of solid state physics and the descriptions of intrinsic properties of materials developed in that discipline. According to solid state theory our physical requirements prescribe a material with a very high valence electron density and with an optical band gap of at least 3.25eV. The high electron density results in a high index of refraction, while a band gap of 3.25eV assures transparency in the optical region. We understand stability as the resistance of intrinsic properties to be altered, or as the resistance of the material against formation of new or additional electronic defect structures.

Our main question is whether those intrinsic properties of a material which make it stable are related to those which make it highly refractive and transparent. As we mentioned, a high valence electron density leads to a high refractive index. Note that we are careful to specify valence electrons because, except for hydrogen and helium, the inner electrons are so tightly bound that they do not participate in any optical processes. Even extreme ultraviolet seldom excites electrons in orbitals whose principal quantum number is less than those of the valence bands. This applies principally to the anion, since the outer electron shell of the cations are very tightly bound--and generally lie one or several tens of eV below the top of the valence band level of the solid. This means that, in general, the same electrons that determine a material's optical properties also determine its stability to ultraviolet radiation. Charged particles, on the other hand, interact principally with the inner shells of electrons; hence the criteria for charged particle stability should be partly independent of those for ultraviolet stability and for ideal optical properties.

In the optical regime it is not only the valence electron density that is important but the distribution of their energy levels and their physical arrangements. Covalent bonding would be the most desirable for both refractive index and for stability. Simple ionic bonds tend to have a greater number of possible defect energy levels in the forbidden band. Covalent bonds have a greater concentration of shared electrons, whereas in ionic bonds the electron tends to be associated mainly with the anion. In Figure 3 we show the band structure of a representative material. The "-E" notation on the figure is conventional, indicating the energy level below the free (vacuum) level. Each line represents a band of energies, which can be split to finer energy separations, as, for example, differences in energy levels of the upper and lower spin states of an electron.

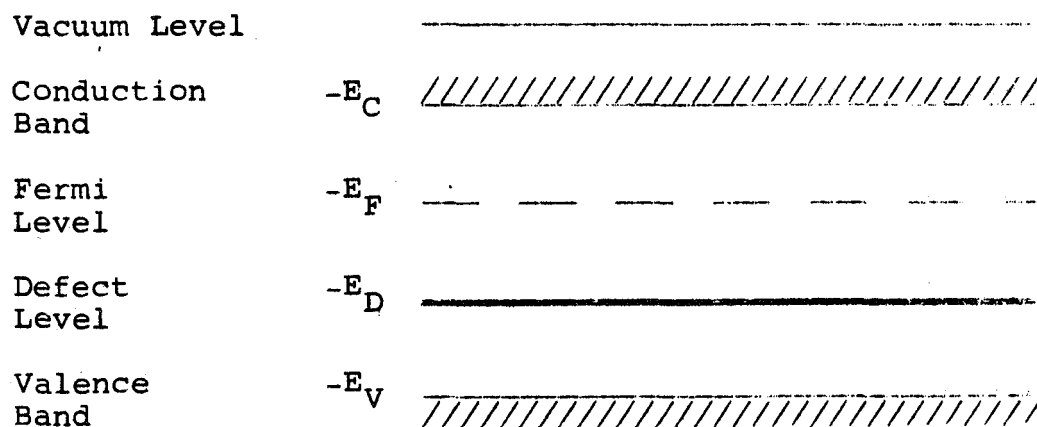


Figure 3. GENERALIZED BAND STRUCTURE OF A DIELECTRIC MATERIAL

If in a material no defects are present, then the population of electrons in the $-E_D$ band will be zero, and the only possible transition of an electron will be from the valence band ($-E_V$) to the conduction band ($-E_C$), a difference of $(E_V - E_C)$, (which for our requirements must be greater than 3.25eV). A photon having an energy greater than the band gap energy, $E_g (= E_V - E_C)$, will

raise an electron from the valence band to the conduction band. The conduction band, in dielectric materials, is essentially empty; the Fermi level (a fictitious level which averages numbers and energies of electrons) in fact is the highest energy level attainable by an electron without external stimulation, and in pure dielectric materials always lies in the band gap. The defect level $-E_D$, whether populated or not, is fixed by its electronic nature; it is usually a level to which an electronic transition is forbidden, but which nevertheless may become populated when the material is ultraviolet-irradiated. When the defect level is populated, however, the Fermi level would also increase if it were not already above the E_D level by at least thermal magnitudes (i.e., $\sim 0.02 - 0.03\text{eV}$). Stability, in a fundamental sense, is determined by the electronic structure, whether this structure will allow or support defect levels, how many, and their probability of population by the action of ultraviolet or charged particles.

4. Inherent Defects - Their Effect on Ultraviolet Stability

If an ultraviolet photon raises an electron to the conduction band, will the material decompose, since this process is equivalent to breaking a chemical bond? From theoretical considerations one would not expect decomposition unless the level $-E_C$ lies very close to the ground level. Removing an electron from the valence band creates a "hole" whose electric field is very strong and which attracts the electron back to it. In the conduction band the electron is mobile; it does not belong to a particular atom. Its lifetime in the conduction band, however, is limited since numerous competitive schemes usually exist for removing it. The distributions and the physical structure of electronic energy levels in solid materials essentially define the various probabilities that an electron will be trapped, will return to the valence band, or will be excited to higher levels.

In real materials there exist at least two gross types of defects--those which are naturally present and those which result from the presence of impurities. Natural defects include cation interstitials, anion vacancies and to a lesser extent combinations or aggregations of these. Impurity defects can exist in a variety of ways--as interstitials, as substitute atoms for anions or cations, as surface adsorbates, etc. When the impurity is substitutional, charge compensation usually increases the concentration of natural defects. For example, when a Li^+ atom is substituted for a Ca^{++} atom, an apparent charge imbalance results because the lithium atom can contribute only one electron to the bond where two are required; consequently, the lithium takes on a negative charge relative to the surrounding lattice. It acts as a defect in two ways; it forms a weaker bond with its neighbors and may also act as a hole trap. The charge imbalance actually is compensated for by an equivalent concentration of anion vacancies so that the net local charge remains zero. Charge compensation therefore increases the concentration of natural defects. The importance of natural defects, whether intrinsic or augmented by impurities, depends upon their energy levels in the band gap. The relationships between electronic structure, the physical arrangement of atoms and the electron bonding between atoms become of paramount importance here not only because some of them determine the intrinsic properties of a material but some also pre-ordain the types of defects which are thermodynamically and electronically permissible. The initial defects influence the initial optical properties and perhaps even the stability to environmentally induced changes; induced defects, of course, profoundly affect stability and obviously may affect solar reflectance.

5. Photolytic Stability

To become somewhat more specific, let us now indicate some of the properties a material should have in order to be both highly transparent and stable. First, it must be a dielectric

with a band gap of at least 3.25 eV and preferably much higher 12 eV on the basis that the zero air mass solar spectrum contains too few photons to break a significant number of 12 eV bonds. Actually, the Franck-Condon principle (Ref. 5) allows us to neglect bond dissociation as a principal mechanism of failure. This principle simply recognizes that electronic processes are orders of magnitude faster than thermal processes; hence an electron raised to an excited state or even to an ionized level has a very much greater probability of returning to its normal state through radiative or other electron transitions than the atoms have of physically separating. This we see to be true on empirical grounds; there are very many examples: x-rays with several tens or hundreds of times more energy than in the basic chemical bonds cause insignificant if any decomposition of dielectric materials; ultraviolet radiation with photon energies much in excess of the band gap energy does not cause decomposition even when there are more than 100 ultraviolet photons absorbed per atom. In short, an electron can and does move much more rapidly than an atom; consequently even though a molecular bond may be broken instantaneously, the electronic relaxation time is so rapid that the atoms involved do not move far enough apart for actual bond breakage before recombination occurs.

For transparency, a 4-8 eV band gap energy suffices but for high index of refraction a high electron density is also necessary. Practically, this means compounds with tightly bound multivalent anions and cations. By "tightly bound" is meant that the bond energies are large, i.e., the bond distances are short and the formation energies are high. Stability considerations suggest that the activation energies for the most probable defects be very high, simply because less defects are likely to result for a given amount of energy absorption. To prevent high concentrations of interstitials and vacancies, the cation and anion should be of comparable size and their separations should be minimal with respect to their respective radii. The electronic structure

should also be such that the ultraviolet absorption coefficient is small; this requires that the energy levels in the conduction band be narrow and discrete with little or no separation between them. Such materials as MgO , Al_2O_3 , ZrO_2 , Y_2O_3 and others meet most of these requirements; all are dielectrics with large band gap energies, low ultraviolet absorption coefficients, and tight atomic structures.

6. Comparative Requirements for Refractivity and for Stability

The interaction of electromagnetic radiation with a solid dielectric material is well documented in the classical and solid state literature (Ref.'s 6 through 8). Briefly, light absorption corresponds to the raising of an electron from one level to a higher one. The polarization which results, however, is very difficult to estimate, the electric field in which the electron jumps obviously is altered when the jump occurs, and the polarization is therefore also affected. The important point, however, is that the polarization induced by the absorption is temporary in that it decays as quickly as the electron returns to its ground state.

This induced polarization persists, however, if the excited state is stable and the electron remains in it. The electron in this "trap" now sets up a field which usually can be described by a potential function of the type

$$E = e/\epsilon r^2 \quad (11)$$

where E is the electric field potential, ϵ , the local dielectric constant, and r is the average separation between the electron and its (effective) neighbors. The dielectric constant, ϵ , has the effect of compressing the energy levels of the free anion. It differs from that of the surrounding medium, ϵ_0 , but the overall effect of ϵ on ϵ_0 may be neglected if the concentration of "traps" is small. The force which keeps the electron trapped, due to actual displacement, is in fact

$$F = \frac{e^2}{r^2} \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon} \right) \quad (12)$$

It is apparent then that the stability of electron (or hole) traps is inversely proportional to the effective dimensions of their orbital radii. A paradox now exists because from a stability point of view, we prefer small atomic separations, yet according to Eq. 12, this promotes greater stability of traps (i.e., it leads to more permanent color centers), although this effect is somewhat diluted by the high dielectric constant. The point is that compromises must be made between properties which lead to high refractivity and those which promote stability. The arrangement of atoms, i.e., the crystal habit, which would be preferred for stability would probably be closer to amorphous than to a definite periodic geometric structure. For high refractivity a regular but compact lattice periodicity is desirable.

7. Activation Energy and Lattice Defects

The absorption due to an impurity or to a stoichiometric defect can be calculated with sufficient accuracy to show how important even trace concentrations of them can be. An impurity can reside in a crystal in several different ways and may exhibit many subtle effects. We can calculate on a simple model the effect of impurities on intrinsic absorption. Consider a material with a band gap energy of 5 eV and assume that the first excited state of an electron trapped at an anion vacancy in this material is 2 eV above the valence band. The anion vacancy is stable irrespective of the trapped electron and if the energy level of the filled trap does not differ much from that of the empty one, we can estimate the absorption as follows: the thermal activation energy we take as 2 eV, assume a density of anions as $\sim 10^{22}/\text{cm}^3$ and a temperature of 20°C. the equilibrium density of anion vacancies is:

$$N_v = 10^{22} \cdot \exp(-2.0/0.025) = 3.5 \times 10^{18};$$

at 100°C. it is

$$N_v = 10^{22} \exp(-2.0/0.032) = 1.9 \times 10^{19}$$

The absorption caused by the above concentrations of defects may be calculated from Dexter's relationship (Ref. 3)

$$K_A = 7.75 \times 10^{-18} N \cdot f \cdot \frac{(n^2 + 2)^2}{ng}, \quad (13)$$

where

K_A = absorption coefficient, cm^{-1}

N = defect density

f = oscillator strength

n = index of refraction of medium

g = damping constant (band halfwidth)

Let us assume $f = 1$, $n = 2.0$, and that $g = 0.5$ eV.

$$K_{20} = (7.75 \times 10^{-18})(3.5 \times 10^{-8}) \left(\frac{(4 + 2)^2}{2(0.5)} \right) = 980 \text{ cm}^{-1}$$

$$K_{100} = 5320 \text{ cm}^{-1}$$

These values of the absorption coefficient correspond to very strong absorption. The K_{20} value results from a vacancy concentration of 350 ppm - a rather large concentration. For an impurity whose electronic properties are similar and whose first excited state is 2 eV above the ground state, the same calculation applies. For an impurity with these same properties then we can expect an absorption coefficient of $\sim 3 \text{ cm}^{-1}$ per ppm. Most high purity pigments have impurities in the range 1-10 ppm and their absorption coefficients therefore become appreciable $\sim 3-30 \text{ cm}^{-1}$. An obvious conclusion here is to obtain the highest purity pigments possible.

The effect of temperature, of course, is very strong. so also is that of the activation energy. For smaller atomic separations (more compact structures) the activation energies

for formation of anion vacancies are somewhat greater, for cation vacancies, they are much greater. Consequently, one would want as compact a lattice as possible, because the activation energies are higher and the physical space for the displaced ion is very much reduced.

8. The Surface State

The discussions above have all been based on dielectric materials with large band gaps, and they have been concerned mainly with bulk properties. In real materials there definitely are effects due to surfaces. The abrupt discontinuity of the dielectric medium makes it necessary for the electric fields to equilibrate differently than they would in the bulk of a crystal. Plainly the smaller the unit particle size the larger is the ratio of the volumes of the accommodation zone and the bulk, the accommodation zone being that zone between the actual surface and that depth in the crystal where the electronic field potentials are no longer sensitive to surface conditions and geometry. If an ion has a wave function which extends over 10 lattice constants, then we would expect the accommodation zone (the "surface") to exist to a depth of at least 25 lattice constants - or $\sim 50-75\text{\AA}$. For a 1-micron-diameter particle, the "surface" accounts for roughly 0.2% of the particle volume. At 0.1 micron this ratio is 1%. At this point it should not be difficult to see that the dielectric constant near the actual surface will decrease. The neighbor and nearest neighbor influences on the polarization of a "surface" atom will depend strongly upon how far the atom is from the surface. The band bending effect derives from this very condition, viz., that the effective dielectric constant and thus the field potential, vary with distance from the surface. The greater the dielectric constant, the more pronounced is this band-bending effect.

Most large band gap semiconductors exhibit very pronounced surface effects because their dielectric constants are very large and thus their "surfaces" extend more deeply into the material

than do those of a dielectric material. Ultraviolet absorption in a semiconductor generally takes place in the "surface" because fundamental absorption is so strong. The very high index of refraction of semiconductors in the visible and near ultraviolet is also associated with the strong fundamental absorption.

The depth to which an ultraviolet photon penetrates in a semiconductor such as ZnO is of the order of 10^{-6} cm, or about 100Å, a depth comparable to that of the "surface." Large band gap semiconductors consequently would not be expected to exhibit ultraviolet-induced bulk effects, an observation which is experimentally true. The dielectric pigments, on the other hand, should degrade almost entirely by color center formation in the bulk, and this conclusion seems also to be experimentally observed; some "surface" effects in dielectric materials would be expected, the number of which should be related to the "surface"/bulk ratio.

The solid state considerations that were discussed in the preceding paragraphs will play a dominant role in establishing the degree of damage that is exhibited by a given pigment. As the particle size decreases, the surface area increases and the probability of surface reactions is enhanced. Furthermore, the greater surface area increases the chances of contamination and impurity-site formation at the surface; also, the work that must be performed to blend pigments into vehicles may further reduce the particle size and/or result in an increase in the structural (lattice) distortions at the surface and in the bulk.

All surfaces, irrespective of crystal nature, possess structures which are different from the bulk (interior). Consequently all the crystalline materials will inevitably possess "defect" structures at their surfaces. As Weyl (Ref. 9) notes, it is an empirical fact that all surfaces, because they are the terminations of interior structure, must accommodate the ionic charge imbalance and the abrupt change in dielectric constant at this point. A non-uniform potential field, as exists at a surface, requires different but compensating orientations of the polarization axes

and thus of the ions than does the uniform field in the crystal bulk. Even single crystals will have "defect" surface structures: for example, thin films, many of them "single crystal," have very different electrical properties than bulk materials because of this structure, and they are grown expressly to take advantage of such structures. Weyl also gives detailed theory of the structure of Al_2O_3 , of MgO , and of some alkali halides. In the first two, he shows how the surface structure accommodates the electrical fields by tending to have oxygen atoms at the outer surface and the cations essentially buried beneath them - a configuration explaining the oxygen dependence and electronegative surfaces of these materials.

9. Charged Particle Interactions

Charged particles lose their kinetic energy in interactions with the deeper-lying electronic levels of a medium. As a fast-moving particle approaches an ion lying in its path, part of its energy is transferred through the coulombic field interaction to the electrons of the ion, with the result that it is ejected and/or the electrons are either expelled (the atom is ionized) or they are raised from their ground states to highly excited states. Some of the ejected ions and electrons, in turn, possess sufficient energy to ionize or excite other atoms or molecules. The probability of energy transfer is greatest for multiply-charged, slow-moving particles. The passage of charged particles through matter involves a series of interactions, the nature of which depends upon their initial energy. As the particle slows down, its potential for causing displacements and thus secondary interactions decreases; the probability for direct ionization also decreases with decreasing velocity - until finally only minor excitations will occur. The interactions most important in terms of optical stability and their relative probabilities are of immediate interest. Though the theory of charged particle interactions in solids is extremely complicated, several important theses can be developed here which pertain to stability.

Seitz (Ref. 10) set forth the basic theory of charged particle interactions. and it is on this theory that the following discussions are based. A parameter, ϵ , is defined,

$$\epsilon = \frac{M_e}{M_p} E_p \quad (14)$$

where

M_e = electronic mass

M_p = mass of charged particle

E_p = kinetic energy of charged particle.

This parameter is the energy an electron would have if it possessed the same velocity as the charged particle. The electron kinetic energy which makes its velocity equal to that of a 5 keV proton is, for example, 2.7 eV. There are two broad ranges of energy to consider - the initial energy of the charged particle and the energy it has after one or more encounters. Only when the charged particle is in or above the keV range will atomic displacements be important; below this range electronic excitation and ionization will be the primary mechanisms by which the moving charged particles will lose kinetic energy. The energy exchange in an elastic encounter can be calculated from the expression:

$$E_t = E_p \frac{4\mu^2}{M_p M_1} \sin^2(\theta/2) \quad (15)$$

where

E_t = energy transferred

E_p = energy of moving particle

μ = reduced mass = $\frac{M_p M_1}{M_p + M_1}$

M_p = mass of moving particle

M_1 = mass of stationary atom

θ = angle of deflection of charged particle.

For the case where $M_1 \ll M_p$, the reduced mass becomes simply M_p . The important point is that the fractional energy transfer (E_t/E_p) is smaller, the greater is the mass of the struck atom. The expression (15) holds for particles (charged or neutral) whose ϵ parameter is less than the energy of the first ionization level of the struck atom.

At higher energies where ionization events are possible, the electrons freed in the process can become trapped to form color centers - particularly in the interstitial-vacancy pairs created by displacements. Because of the large difference in energy requirements, ionization events are far more likely, and an estimation of energy loss rates gives a fair approximation of ionization rates.

For these more energetic reactions, in which the particle velocity greatly exceeds the orbital electron velocities in the struck atom, we can use the expression:

$$\frac{-dE}{dx} = \frac{4\pi z^2 e^4}{M_e v_p^2} N_o Z \log(\hat{\epsilon}/B) + \frac{2\pi z^2 e^4}{\hat{\epsilon}} Z_i \log(\hat{\epsilon}/B_i), \quad (16)$$

where

$\frac{dE}{dx}$ = the energy loss per unit distance per incident particle

z = number of charges on the charged particle

e = electronic charge

M_e = electronic mass

v_p = velocity of charged particle

N_o = density of stationary atoms

Z = atomic number of stationary atoms

B = a parameter characteristic of the electronic energy structure of the stationary atoms (of the order of the ionization potentials)

Z_i = number of electrons per atom in the outer shell, and

B_i = an energy parameter characteristic of that shell (similar to B).

The energy loss spent in displacement of atoms per incident charged particle can be calculated from

$$\frac{-dE}{dx} = \frac{2\pi z^2 Z^2 e^4 N_o}{MV_p^2} \log\left(\frac{E}{E_D} \cdot \frac{4\mu^2}{mM}\right) \quad (17)$$

where

m = mass of the charged particle, and

M = atomic mass of stationary atom.

The displacement energy, E_D , is the minimum energy which must be transferred to an atom to eject it from its lattice site.

Equations 16 and 17 show that the rate of energy loss is directly proportional to: material density, charge on the moving particle, and the atomic number of the stationary atom; and that it is inversely proportional to: the energy of the moving particle, and, in the case of displacements, to the mass of the stationary atom, and the displacement energy. The rate of displacement can be calculated from Eq. 17 and a knowledge of the rate of charged particle incidence and the displacement energy. This gives a rough idea of the instantaneous rate of formation of interstitials and vacancies (potential color centers).

The atomic number and the valency of the atoms in a target material turn out to be the most important parameters. Hence, we would like materials whose atoms are of high atomic number and of single valency. Earlier we indicated that multivalent systems generally promote higher refractivities; so it appears that a compromise is necessary for charged particle applications. Since the z and Z terms in the above expressions are squared, the energy loss would be very sensitive to valency. Even though more thought should be given to these considerations, it is evident that certain of the parameters decrease energy loss rates but affect the optical properties negatively, and here too compromises must be made.

Not discussed above were the fates of displaced ions and electrons. It is a fortunate fact that the actual induced vacancy

and interstitial concentrations of irradiated materials are orders of magnitude less than those calculated from theory; this is because the displaced atoms/ions eventually return to the vacancies they generated. The estimation of induced vacancy and interstitial concentrations therefore bears little relation to the actual permanent concentrations of these defects.

F. Discussion

In comparing the properties of a material which confer upon it high optical transmission and refractivity with those which confer stability, we find some which are complementary and several which are not. Much more detailed attention is deserved in this area. We have attempted here mainly to introduce the question, to describe its important aspects, and to show the necessity to make compromises.

A clear and convincing rationale for selection and subsequent treatment of ultraviolet-stable pigments is not available; if it were, it would undoubtedly be inconsistent with a similar rationale pertinent to materials for charged particle environments. We are firmly convinced, nonetheless, that an in-depth study should be made of the criteria for optical stability with specific reference to the effects of the ultraviolet and charged particle environments of outer space.

As we have attempted to illustrate, the concept of three independent but related models comprising a general model offers a significant method by which to understand empirical behavior of thermal control coatings from a theoretical point of view. Some of the parameters which determine spectral reflectance are altered in interactions with energetic radiations; some are not. Their influence and the amount of property change induced by the external environment bear directly on the amount of spectral damage incurred. The index of refraction, an intermediate parameter, quite obviously has an important place in at least two of the models. The induced absorption likewise contributes

importantly to the general model. Eventually, when the relationships which exist between the individual models become known, those between the parameters will also become more clear.

As the analyses show, a dielectric material with low solar absorptance (and high infrared emittance) should have a band gap just large enough to be transparent to the bulk of the solar spectrum (i.e., ~ 4 eV or greater). To have a high index of refraction it should have covalent bonding and a close-packed molecular structure. Stability to ultraviolet requires that the material have as large a band gap as possible; this, however, reduces the refractive index in the visible region. Stability to ultraviolet also requires that all intrinsic defects have high formation energies and low mobilities. For stability to charged particle radiations, the material should be made up of elements with high atomic weights. The latter will resist displacement reactions which could result in a much increased density of interstitials and vacancies (I-V pairs). Once created these I-V pairs would, from our ultraviolet stability considerations, be stable. Hence there would seem to be a compromise necessary, especially for missions involving considerable exposure to high energy charged particles (e.g., Van Allen Belt or Jupiter's Magnetosphere).

The properties most desirable from an ultraviolet stability viewpoint may not be compatible with those for initial properties or stability in other environments. In the choice of possible materials there exists a wide range of the important parameters. For any single material comparatively little adjustment can be made in these parameters. In any case, it is important to identify those basic parameters which determine initial optical properties and those which influence the optical damage sustained in various environments, and most importantly to identify those which are common.

III. REFLECTANCE THEORY AND EXPERIMENTS

A. Introductory Remarks

The interactions of radiant energy with finely divided materials are in general so complicated and so poorly understood that the theoretical treatment of such interactions usually involves many very limiting and exclusive qualifications. In introducing this section of the report we would like to present some background to the theory and experimental work in light scattering and to show how light scattering as a science applies to stable, pigmented, thermal control materials.

Low solar absorptance, pigmented, thermal control materials, by definition, must utilize finely divided pigment materials dispersed, for practical reasons, in a suitable binder material. The successful attainment of coatings with very high solar reflectance and high thermal emittance requires that the least absorptive (most transparent) materials be used. The various scattering theories which exist (Mie in particular, Rayleigh, Debye, etc.) all require a particle size roughly of the same dimensions as that of the wavelength of light to be reflected. A spherical particle with a diameter of one micron, for example, will have a higher scattering cross section for visible light, according to Mie theory, than one with a 10 cm diameter. The point is that a dielectric material, to be highly reflective, must be both transparent and finely divided. Unfortunately, the finely divided state of a material obviously brings with it a large surface area, and a correspondingly large amount of surface activity. In this sense the major problems are in obtaining sufficiently transparent materials and in maintaining (stabilizing) this transparency in the finely divided state. In this section, however, we are interested only in the light scattering aspects of the problem.

In engineering terms we have come to know well the expression:

$$\alpha + \rho + \tau = 1 \quad (18)$$

Here α is the absorptance; ρ , the reflectance; τ , the transmittance; and all are the spectral hemispherical values at wavelength λ . Equation 18 is a completely valid thermodynamic law; it accounts spectrally for all the radiation energy incident on a material. The important point is that these terms represent different radiative interactions and that the energy accounting is done on a directional basis. By definition any radiation striking a surface and returning in the same general direction from which it came is called reflected radiation. Radiation passing completely through a material is referred to as transmitted radiation. In a moderately reflecting but transparent system, some radiation entering it will be scattered out of the system in the forward direction and the remainder, apart from that absorbed, will be scattered out in the opposite direction. By the term "scattering" we mean any change of direction of a beam of light through refractive or diffractive processes; it does not include absorption and subsequent re-radiation at a different wavelength. The thermodynamic laws do not distinguish between processes. In a scattering system the processes which operate to make a system transparent are the same as those which make it reflective, and one can say that reflectance in such cases is transmittance in the opposite direction.

An individual photon of radiation incident on a material is either absorbed or not absorbed. Those photons which are absorbed are accounted for by the term α ; those not absorbed are accounted for according to the direction the individual photons ultimately take. The basic point is that reflectance and transmittance imply non-absorptive processes and are essentially identical, except for the directions of their emergence from a material with respect to direction of incidence.

B. Absorption in Multiple Scattering Systems

In a white paint the high visual reflectance is achieved by a combination of low absorption (i.e., very high intrinsic transmittance), and multiple scattering results from the total effect of dispersing micron size pigment particles in a binder (vehicle). The ratio of the index of refraction of the pigment to that of the vehicle (n_p/n_v) and the ratio of particle size to wavelength (d_p/λ) bear importantly on the reflection efficiency. The actual magnitude of reflectance and its variation with wavelength, and especially as these are affected by particle size and shape distributions, have never been satisfactorily treated in multiple scattering systems.

What is necessary in this work is that the scattering processes be independent of induced absorption. Thus, so long as particle physical statistics remain unaltered and as long as the induced defects do not significantly alter the index of refraction either of the pigment or the vehicle, the scattering properties will be constant.

Analogous to transmittance measurements, reflectance of "opaque" paint coatings is determined by comparing the incident and emergent intensities, in this case the reflected radiation intensity. In a single crystal a small part of the incident radiation is reflected from the crystal surface in accordance with Fresnel's law, i.e.,

$$R_F = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (19)$$

If $k \ll n$, Eq. 19 can be written:

$$R_F = \frac{(n - 1)^2}{(n + 1)^2} \quad (20)$$

For representative dielectric materials $n \leq 2.0$, and $R_F \leq 0.1$. In exceptional cases R_F may be greater. However, this calculation is misleading because Fresnel reflection occurs only

at the specular angle and, integrated over the whole 2π plane of reflection, it contributes very little to the total diffuse reflectance. By the same token, even if the induced defect concentration, N_i , were to affect n , its ultimate effect on diffuse reflectance would be mitigated by the above considerations.

A white paint (comprised of transparent particles dispersed randomly in a transparent vehicle) reflects light by causing it to be reflected and refracted at a multiplicity of sites within the paint film. A photon will engage in numerous scattering events before it will eventually emerge as a "reflected" photon. As long as the total cross-section for scattering greatly exceeds that for absorption, the reflectance will have a high value. If, in the random path that a photon takes, the number density of absorbers, i.e., the absorption cross-section, increases, then the reflectance will decrease. The situation can be represented mathematically. Let σ_s be a monochromatic scattering cross-section, arbitrarily defined to include all types of scattering events; σ_a a monochromatic absorption cross-section, arbitrarily defined to include all absorptions - in the vehicle and in the pigment. If there are N_s scattering centers per unit area of reflecting surface, and N_a absorbing centers per unit area of reflecting surface, the total effective scattering cross-section is

$$\Sigma_t = N_s \sigma_s - N_a \sigma_a = \Sigma_s - \Sigma_a \quad (21)$$

We now assume that the reflectance is given by the expression

$$R = R_o \exp(\Sigma_t) = R_o e^{\Sigma_s} e^{-\Sigma_a} \quad (22)$$

The actual form of the expression is not important, but one can see that, if Σ_s is unaffected by changes in σ_a , then the net loss in reflectance due to N_a absorbing centers depends partly upon whether σ_a is larger or smaller than its corresponding value in the same material where scattering is not present. It depends also upon the distribution of the N_a absorbers within the

paint film - whether they are created at depths greater or lesser than the thickness for reflectance opacity in the wavelength region where the N_A absorbers are effective.

C. Light Scattering Theory

The reflectance of finely divided materials, aside from being a poorly understood phenomenon, is generally termed "light scattering" and it is a difficult process to describe. In simplest terms, it is the process by which a finely divided material returns incident radiation in the general direction from which it came. The purpose of this section is to present very briefly the various theories of reflectance from highly scattering media and discuss their relevance to this program.

Maxwell's equations form the basis of all classical electromagnetic theory and also the foundation for most current reflectance theory. Historically, reflectance theory was first developed by Snell and then by Fresnel (for an excellent review, see Ref. 6), who solved Maxwell's equations with the boundary conditions that the electric vector of the incident electromagnetic wave be continuous at the surface. Rigorous solutions were obtained which fitted experimental data quite well. All of these theories, however, assumed the dimensions of the electromagnetic wave to be very small compared to those of the material's surface orthogonal to the direction of the wave. Thus, reflectance theories usually work well for plane, homogeneous surfaces of semi-infinite extent.

As the dimensions of the material approach those of the electromagnetic wave and as the geometry departs from planar, classical theory becomes much more difficult to apply. The best known and still most widely used theory of particulate scattering is that due to the Mie (Ref. 11). Mie theory (see also Sinclair and LaMer, Ref. 12) applies strictly to non-absorbing spherical particles, and in practice to particles separated at least several particle diameters. The scattering coefficient, K , in Mie theory is defined by the series:

$$K(\alpha, n) = \frac{2}{\alpha} \sum_{j=1}^{\infty} (2j + 1) \left[|a_j|^2 + |b_j|^2 \right] \quad (23)$$

where

$$\alpha = \frac{2\pi r}{\lambda}$$

r = particle radius

λ = wavelength

$$a_j = (-1)^{j+1/2} \frac{S'(\beta)S(\alpha) - nS'(\alpha)S(\beta)}{S'(\beta)\Phi(\alpha) - n\Phi'(\alpha)S(\beta)}$$

$$b_j = (-1)^{j+3/2} \frac{nS'(\beta)S(\alpha) - S'(\alpha)S(\beta)}{nS'(\beta)\Phi(\alpha) - \Phi'(\alpha)S(\beta)}$$

$$\beta = n\alpha$$

n = index of refraction at wavelength λ

$$S(x) = \left(\frac{\pi x}{2}\right)^{1/2} J_{(j+1/2)}(x)$$

$$\Phi(x) = S(x) + iC(x)$$

$$C(x) = (-1)^j \left(\frac{\pi x}{2}\right)^{1/2} J_{(-j-1/2)}(x)$$

The J terms are Bessel functions of an order indicated by their subscripts. The S' terms are derivatives with respect to the indicated argument. To calculate the angular distribution of scattered initially unpolarized radiation, the relationship is

$$I(\theta, n) = \frac{I_0}{2} (i_1 + i_2) \quad (24)$$

Where θ is the angle between the incident and scattered beam, I_0 the incident beam intensity, and i_1 and i_2 are intensity functions defined as follows:

$$i_1 = \left| \sum_{j=1}^{\infty} \frac{2j+1}{j(j+1)} (a_j \eta_j + b_j \zeta_j) \right|^2 \quad (25)$$

$$i_2 = \left| \sum_{j=1}^{\infty} \frac{2j+1}{j(j+1)} (a_j \pi_j + b_j \pi_j') \right|^2 \quad (26)$$

and π_j is the derivative of the corresponding Legendre Polynomials of order j ; that is,

$$\pi_j = \frac{dp_j}{dx};$$

and

$$\gamma_j = \pi_j (\cos\theta - \sin^2\theta)$$

These formulae are presented here mainly to indicate the extreme complexity of calculations of Mie scattering coefficients. The series in some cases must be taken to very high indices to obtain satisfactory convergence. Iterations must be made for each particle size, wavelength, index of refraction, and scattering angle.

In a system in which the incident light beam interacts on average with only one particle, single scattering predominates. When the system size becomes large (many particles thick) or the particle spacing becomes small with respect to particle size (mean free photon path $\ll$ system dimensions), then the probability becomes great for more than one scattering event per photon. Consequently in thick or dense systems multiple scattering takes place. The computational complexity of solving the Mie equations for not only the distribution of the scattered radiation from the incident beam but also that from the first and succeeding scattering events becomes exceedingly great. In secondary and succeeding events the radiation incident on a particle thus comes from random directions rather than from the original direction.

In addition to the computational complexity, however, there is an interaction between particles in which the surface forces and fields of each particle have a mutual effect, one upon another. As the separation between the particles decreases, the

interaction effect becomes larger. When the particles touch, the surface forces on each will cause them to stick together, and it may be a moot question whether the system behaves as two individual particles or as a single larger particle. One would also expect that these surface forces - Van der Waal's forces - would be proportionately greater with decreasing particle size (Ref. 13).

D. Theoretical and Experimental Results in Light Scattering in Optically Dense Dielectric Media

Churchill, Clark and Sliepcevich (Ref. 14) found that the limiting center to center distance above which interference could be correlated was 1.7 particle diameters (for relatively inert latex spheres). The data of Sarofim et al (Ref. 15) indicated that, when particle separations become smaller than about 2 particle diameters, interference effects become very important, effectively reducing the expected Mie scattering crosssection. Measurements of the scattered intensity at seven (7) wavelengths for angles of incidence from 0° to 180° , compared to those expected from Mie theory definitely indicated interference effects with decreasing particle separation, d_p . The authors suggest that both d_p/λ and d_v/λ criteria are important, where d_v is the inter-particle distance (average void size). Van de Hulst (Ref. 16), in the introduction to his book "Light Scattering by Small Particles," definitely excludes all systems in which the particle separation is less than several particle diameters but does not explain his reasons. Suffice it to say that as particle separation is reduced to dimensions of the order of the wavelength of the incident wave, calculational complexity becomes extreme and theory apparently breaks down rather seriously.

The extreme complexity of Mie theory has prompted many scientists to search for and/or invent simpler formulations of light scattering theory. We will review briefly a few reflectance theories which deal with highly reflecting systems. One should note that the theory of light scattering in optically dense

media is inadequately developed in at least one major respect, and the treatment of it is largely phenomenological. The first breakthrough in attaining a relatively simple theory for dense systems was due to Kubelka and Munk (K&M), who solved a system of simultaneously differential equations for the backward and forward radiation intensities (Ref. 17). The reflectance of the film was then stated as a function of S, the scattering cross-section; K, the absorption crosssection; and X, the thickness. Particle geometry was not a part of K&M theory. Still, K&M theory was complicated and difficult to work with. Kubelka (Ref.'s 17, 18) simplified K&M theory by considering special cases and relaxing some of the restrictions in the original theory. He derived practical formulae using S and K for calculating reflectance with and without backing and in non-homogeneous layers. Unfortunately, the K&M coefficients, S and K, must be measured experimentally, and hence all K&M theory and modifications of it require a-priori measurements; their main utility is in obtaining comparative data.

Others who have studied light scattering include Gurevic (Ref. 19) and Judd (Ref. 20), both of whose theories, according to Kubelka (Ref. 18) are in good agreement with Kubelka's simplified K&M theory. Brillouin (Ref. 21) applied rigorous classical theory to show why, in the case of large d_p/λ , the theoretical scattering crosssection is twice the actual crosssection. Heller and Pangonis (Ref. 22) solved the Mie equations for specific conditions; and their results imply that the "maximal specific scattering power" for a given material and wavelength is larger the smaller the particle size provided the relative refractive index is increased correspondingly. This conclusion appears similar to Jaenicke's relationship (Ref. 23):

$$d(\lambda) = \frac{0.90}{n_p''} \cdot \frac{(m^2 + 2)}{(m^2 - 1)} \cdot \lambda \quad (27)$$

where

$$m = n_p/n_v$$

n_p = refractive index of pigment

n_v = refractive index of vehicle.

This relationship determines the optimum pigment particle diameter for maximum reflectance at a wavelength λ when the indices of refraction of the pigment and of the vehicle are n_p and n_v , respectively. Butler (Ref. 24) extended and made more practical the K&M theory by showing that the S&K coefficients and the "reflectivity" of an infinitely thick system of particles can be obtained by transmission measurements. An apparent conflict, however, exists between Butler's findings and those of Kubelka (Ref. 19) in that Kubelka shows theoretically and experimentally that spectral reflectance and absorptance of a non-homogeneous specimen depend on direction of illumination whereas spectral transmittance does not. The important results of Butler's work are a theoretical proof that scattering intensifies absorption and provide an experimental confirmation of it. Furthermore, his data clearly indicate that the intensification is much greater when the absorbing material is adsorbed on or chemically bound to the scattering media than when simply admixed with it.

There are numerous other works which relate similar results, both theoretical and experimental. None, however, really provide much "theoretical insight;" most, by a large margin, treat the problem strictly from a phenomenological point of view. Those which treat the theory, e.g., Rayleigh (Ref. 25) and Strutt (Ref. 26) do not do so in terms of fundamental materials properties. An excellent and comprehensive review of the theory of classical electromagnetic scattering has been given by Stratton (Ref. 6). On the practical side, Sinclair and LaMer (Ref. 12) have published a classic paper - one which reviews light scattering theories, discusses them, and relates theory and practice in the optics of fogs and hazes. They also give experimental data.

IIT RESEARCH INSTITUTE

The earliest work relating directly to spacecraft thermal control coatings was performed at IITRI; it was reported by Moore et al (Ref. 27) and by McCully et al (Ref. 28). These reports reviewed classical theory in electromagnetic radiation interactions, gave the mathematical derivation of Mie Theory, and pointed to the importance of particle size and size distribution. The theory of Jaenicke (Ref. 23), for example, as embodied in Eq. 27, was discussed at some length, particularly in the determination of optimum particle size distributions. In later work (Ref. 29), IITRI conducted basic light scattering investigations. Models of reflectance in highly pigmented systems were experimentally tested. The major conclusion was that theory seemed to work well in dilute systems but not in concentrated ones. An "ideal coating" consisting of several layers of ever-decreasing particle size was proposed. This program also included studies of statistical models of light scattering, when the failure of Mie Theory to be of any assistance was recognized. Monte Carlo and random-walk models were developed to study energy penetration and cluster growth, respectively, in a paint film.

In concluding this section we would like to note that very little information or data relating the reflectance of multiple scattering systems to scattering theory could be found. The dependence of scattering crosssections on wavelength, particle size, particle separation, refractive index and/or refractive index ratio, according to any current theories, must be determined experimentally. The explanations, of course, are several, but the chief one seems to be that the basic optical constants, n and k , take on effective values when surface forces are substantial, and the magnitudes, spectrally and spatially, of these effective values (with respect to their values in bulk materials) are not known as a function of particle geometry. In terms of their relevance to this program, the more pragmatic theories offer at best a phenomenological explanation with little, if any, insight.

The more fundamental theories, of course, have not been successfully applied to or tested in intensely scattering or optically thick particle systems.

IV. A THEORETICAL ANALYSIS OF THE DEGRADATION OF SOLAR ABSORPTANCE IN LOW α_s/ϵ THERMAL RADIATIVE COATINGS

A. Introduction

Since the earliest use of "white paints" on earth orbiting spacecraft, a considerable amount of research and development has been devoted to attaining coating systems not just of very high reflectance (to solar radiation) but with good stability (resistance to solar ultraviolet and charged particle radiations). Considerable progress has been made except in the area of the prediction of thermal radiative performance, that is, of space environment effects. In this section the theory of induced solar absorptance changes is developed from theoretical considerations. The treatment starts with the derivation of the Lorenz-Lorentz dispersion equation, and extends this equation to multiple scattering systems; the change in solar absorptance, $\Delta\alpha_s$, as a result of the induction of a given concentration of a specific type of defects is then obtained. Finally, the general time dependence of solar absorptance degradation is developed and discussed using several models of the kinetics of defect ("color center") growth.

B. The Oscillator Model

In the classical treatment of an electron in a periodic electric field (Ref.'s 3, 5 and 6) the displacement, x , of an electron from its mean position, by virtue of its charge, e , produces a polarization of magnitude ex . In a periodic electric field the polarization would of course vary with the frequency of the field. The electron would experience acceleration forces equal to $m\ddot{x}$, a damping force proportional to its velocity, $mg\dot{x}$, and a restoring force proportional to the distance through which it is displaced from its mean position, $\omega_o^2 x$. The latter term, with ω_o^2 , is used for convenience in the mathematical solution. All of these forces must be equal to the instantaneous value of the applied electric field. The electron's motion in a periodic electric field whose intensity is $E = E_o \exp(i\omega t)$ is described by

$$m\ddot{x} + mg\dot{x} + \omega_0^2 x = E_0 e^{i\omega t} \quad (18)$$

The solution to Eq. 18 is

$$x = \frac{e}{m} \cdot \frac{1}{\omega^2 - \omega_0^2 + i\omega g} \quad (19)$$

The polarization, P , is equal to ex ; for N electrons if it is Nex , so that Eq. 19 can be written

$$P = Nex = \frac{Ne^2}{m} \cdot \frac{1}{\omega^2 - \omega_0^2 + i\omega g} \quad (20)$$

The induced polarization increases the complex dielectric constant according to the expression:

$$\epsilon = \epsilon_0 + 4\pi P = 1 + \frac{4\pi Ne^2}{m} \cdot \frac{1}{\omega^2 - \omega_0^2 + i\omega g} \quad (21)$$

The complex dielectric constant in more rigorous treatments is related to the polarization in a more complicated way than expressed in Eq. 21. Instead of ϵ , the expression $(\epsilon + 2)/(\epsilon + 1)$ is sometimes suggested. However, for the present development the simpler expression is quite adequate. Since the complex index of refraction n^* is defined by $n^* = n - ik$ and since the dielectric constant equals the square of the complex index of refraction, ($= n^{*2}$),

$$n^2 - k^2 = \epsilon_0 + \frac{4\pi Ne^2}{m} \cdot \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \omega^2 g^2} \quad (22)$$

$$2nk = \frac{4\pi Ne^2}{m} \cdot \frac{\omega g}{(\omega_0^2 - \omega^2)^2 + \omega^2 g^2} \quad (23)$$

The important quantity is the extinction, $2nk$. The meaning of extinction is that a monochromatic, mono-directional electromagnetic beam, passing through a material of unit thickness and

with a $2nk$ value of 1 will be degraded in intensity from I_0 to I_0/e . Extinction, however, does not necessarily mean that the beam energy is absorbed; it in fact accounts also for the energy scattered out of the (mono-directional) beam. If, however, n remains essentially unchanged for reasonable values of N , then $k(N)$ represents true absorption. The point may be made clear by comparing Eq.'s 22 and 23 for given values of N , ω , ω_0 and g . Assume $N = 10^{18}$, $\omega = 4.0 \times 10^{15}$ rad/sec ($\lambda = 0.47\mu$), $\omega_0 = 3.76 \times 10^{15}$ rad/sec ($\lambda = 0.5\mu$), and $g = 0.6 \times 10^{15}$ rad/sec ($= 0.45\text{eV}$). If $\epsilon_0 = 6$, $n^2 - k^2 = 6 + 6.58 \times 10^{-4}$, or $\Delta n \approx 0.0257$, if $k \ll n$; and, if $n \approx (\epsilon_0)^{1/2}$, $k = 1.41 \times 10^{-4}$. The absorption coefficient K is then equal to $4\pi k/\lambda = 37.4 \text{ cm}^{-1}$, an appreciable amount of absorption. Large concentrations of defects would be required to affect substantially the refractive index, while the same concentrations very appreciably effect the absorption coefficient.

A rigorous treatment of absorption by quantum mechanics (Ref. 4) leads to exactly the same expression as Eq. 21; in the quantum mechanical sense, however, the quantity m is interpreted as an effective value of the electronic mass, designated m^* . A factor f , the oscillator strength, is added to account for the fact that not all defects of a specific type can participate in absorption. The factor g is the damping constant (measured width of the k vs ω curve); it is a measure of the effective widths of the energy bands between which an electronic transition takes place. In other words it reflects the number and width of the allowed energy levels in the states from and to which an electron jumps in the absorption act. The center frequency, ω_0 , is determined by the mean energy separation of the states.

A better understanding of these factors can be gained by referring back to Figure 3, which is a conventional energy level diagram. The region between E_V and E_C is known as the forbidden band. Transitions from the valence (filled) band ($E < E_V$) to states in the forbidden band are not allowed. If, however, the electronic configuration is altered locally, then new electronic

energy levels are created, and such transitions may become allowed. Thus, if a defect is created in the lattice of a crystalline material, or a free radical in a polymeric compound, the local electronic structure becomes distorted enough that one or more discrete energy states are created in the forbidden band. As Figure 3 shows, the introduction of an energy state E_D now gives rise to a possible absorption characterized by an ω_0 corresponding to $\omega_0 = (E_D - E_V)/2\pi\hbar$. Another transition which is also possible is that from E_D to E_C , characterized by a center frequency of $\omega_0 = (E_C - E_D)/2\pi\hbar$. In this picture it should be made clear that transitions from E_D to E_C will depend upon how populated the state E_D is, which will in turn depend upon the statistics of the $E_V \rightarrow E_D$ transition and the intrinsic stability of the E_D state. One further point is that upward transitions to states in the forbidden band are strongly forbidden. Transitions from the conduction band (fluorescence) to those states are, however, usually allowed.

The important points to remember are that each defect has characteristic values of ω_0 and g which determine the absorption band shape, and that the magnitude of the induced effect (optically) depends upon N , f and m^* . Rewriting Eq. 23 the form of the desired expression is

$$k(\omega) = \frac{2\pi N_i e^2 f_i}{n(\omega) m_i^*} \cdot \frac{\omega g_i}{(\omega_{0,i}^2 - \omega^2)^2 + \omega^2 g_i^2} \quad (24)$$

If there are l number of different types of defects, then

$$k(\omega) = \sum_{i=1}^l \frac{2\pi N_i e^2 f_i}{n(\omega) m_i^*} \cdot \frac{\omega g_i}{(\omega_{0,i}^2 - \omega^2)^2 + \omega^2 g_i^2} \quad (25)$$

In a more general notation

$$k(\omega) = \sum_{i=1}^l \frac{2\pi}{n(\omega)} \frac{N_i e^2 f_i}{m_i^*} \cdot F(\omega_{0,i}, g_i) \quad (26)$$

where the assumption is made that $n(\omega)$ is insensitive to N_i . The function of $F(\omega_{0,i}, g_i)$ is quite general and can represent any shape. In many cases, the shape of the induced absorption band is not Lorentzian (Eq. 23) but Gaussian, i.e.,

$$2nk(\omega) = -\frac{4\pi N_i e^2 f_i}{m_i^*} \cdot \exp \left[-(4\ln 2)(\omega - \omega_0)^2 / g_i^2 \right] \quad (27)$$

Each optically active defect in a material has its own characteristic shape, and in a material with several such types of defects several different band shapes may be present.

For reference, the value of $4\pi e^2/m$ is 3.182×10^9 when ω and g are expressed in radians/sec. If ω and g are in eV units, then it is $= 1.379 \times 10^{-21}$. These values must be multiplied by oscillator strengths, f_i , and divided by the ratio of effective masses, m_i^* , to the rest mass, m_e , of an electron. For real materials oscillator strengths are rarely unity and effective electron masses are usually not equal to rest mass values. The factor A_i will be used to denote the term $4\pi e^2 f_i / m_i^*$; and the factor F_i , the band shape. Thus we have, in simplified notation, $2nk(\omega) = A_i \cdot F_i \cdot N_i$.

C. Defect Induced Changes in Solar Absorptance

The solar absorptance of a paint system is defined as

$$\alpha_s = \frac{\int_0^\infty \alpha_\lambda S_\lambda d\lambda}{\int_0^\infty S_\lambda d\lambda} \quad \text{or} \quad \frac{\int_0^\infty \alpha_\omega S_\omega d\omega}{\int_0^\infty S_\omega d\omega} \quad (28)$$

If in this case α_ω represents an induced absorption, then we would have

$$\Delta \alpha_s = \frac{\int_0^\infty \alpha_\omega S_\omega d\omega}{\int_0^\infty S_\omega d\omega}, \quad (29)$$

where S_ω is the spectral energy distribution in the solar spectrum. In conventional units absorption is represented by $K(= 2ck)$ or $(4\pi k/\lambda)$. It is necessary now to imagine that the reflecting layer is a transmitting system (which in a sense it really is). The problem with this analogy is that the connection between transmittance path length and reflectance path length is obscure at best. So, an empirical "scattering factor," $C_s = C_s(\omega, x)$ is introduced, such that actual absorption is measured by $e^{-C_s K x}$ and $K = k(N_i \cdot \omega \cdot g_i \cdot \omega_{O,i})$.

In practice the spectral transmittance of an homogeneous material is determined by the ratio of I/I_0 . A quantitative measure of its absorption can be obtained from $\log_e I/I_0 (= -Kx)$. A spectrophotometer operated in the optical density (O.D.) mode thus plots the quantity Kx . Therefore, if x is known, then K can be calculated from $K = \text{O.D.}/x$. Frequently the number density of absorbers can be determined, the quantity k being directly proportional to the number of absorbers in the light path - at a particular wavelength. The analogous process can be applied to white paint systems. By analogy, the reflectance degradation becomes:

$$(\text{O.D.})_R = \log_e \left(\frac{R_0}{R} \right) = ak \quad (30)$$

where

$$\begin{aligned} a &= 2C_s \cdot x \cdot \omega / c \\ c &= \text{speed of light, and} \\ x &= \text{film thickness.} \end{aligned}$$

Rewriting Eq. 30, the degraded reflectance is:

$$R = R_0 e^{-ak} \quad (31)$$

and the change in reflectance is:

$$\Delta R = R_0 (e^{-ak} - 1) \quad (32)$$

The absorptance change is $-\Delta R$, hence

$$\Delta\alpha = R_o (1 - e^{-ak}) \quad (33)$$

Now, the solar absorptance change will be:

$$\Delta\alpha_s = \frac{\int_0^{\infty} R_o(\omega) \left[1 - e^{-ak(\omega)} \right] S(\omega) d\omega}{\int_0^{\infty} R_o(\omega) S(\omega) d\omega (= S)} \quad (34)$$

Inserting the previous results in 34 provides the more general relationship:

$$\Delta\alpha_s = \frac{1}{S} \int_0^{\infty} R_o(\omega) \left[1 - \exp \left\{ -a \sum_i k_i(\omega) \right\} \right] S(\omega) d\omega \quad (34a)$$

Alternatively, it can be written:

$$\alpha_s = \alpha_{s,o} + \frac{1}{S} \int_0^{\infty} R_o(\omega) \left[1 - \exp \left\{ -a \sum_i k_i(\omega) \right\} \right] S(\omega) d\omega \quad (35)$$

The discussions which follow may have more meaning if some representative numerical values are given. For the sake of illustration we will use properties typical of dielectric materials such as Al_2O_3 , SiO_2 , ZrO_2 , etc. Most of these have optical absorption bands induced in them at wavelengths around 0.35μ (3.5 eV) with bandwidths of the orders of 0.5 eV. To calculate the attenuation in reflectance at this wavelength, we will assume the following: a scattering factor, $C_s = 10$; a film thickness, $x = 0.01$ cm; an index of refraction, $n = 1.6$; and an induced defect density, $N_i = 10^{16}$ defects/cm³. The quantity a ($= 2C_s \cdot x \cdot \omega/c$) has a value of about 1.85×10^5 at $\lambda = 0.35\mu$ ($\omega = 5.6 \times 10^{15}$ rad/sec). The term F_i , evaluated as a Lorentzian bandshape at $\lambda = 0.35\mu$ (3.5 eV) with $g = 0.5$ eV, is about 0.53, so that k ($= A_i F_i N_i / 2n$) has a

value of 4.3×10^{-6} . The product ak then has a value of roughly 0.8. The resulting attenuation, $e^{-0.8}$, is 0.45, and the reflectance at this wavelength is degraded to 55% of its original value. The effect of scattering is particularly noticeable, as is that of the defect density. The rate of production of defects is another quantity we would like to appreciate numerically. It depends upon the incidence rate of damaging photons, the atomic capture (absorption) cross-section, the number density of atoms, the cross-sectional area, and the quantum efficiency (probability that a defect will form per absorbed photon). In near earth solar radiation the flux of photons of energy greater than 4 eV ($\lambda \leq 3000\text{\AA}$) is roughly 2×10^{16} photons/cm²-sec. The macroscopic absorption coefficient in this spectral region of dielectric materials is of the order of 10^3 cm⁻¹, which implies a microscopic (atomic) absorption coefficient of 10^{-19} cm² (i.e., $K/N_0 \sim 1000$ cm⁻¹/10²² absorbing atoms per cm³). The number density of atoms, N_0 , is roughly 10^{22} times the film thickness, or for $x = 0.01$, $N_0 = 10^{20}$ atoms/cm². We use unit cross-sectional area; and assume the quantum efficiency, η , is of the order 10^{-4} . Then $B = I \cdot \sigma \cdot N_0 \cdot 1 \cdot \eta = 2 \times 10^{13}$ defects/sec. For threshold damage energies greater than 4 eV, B drops off sharply. At 6 eV, I is approximately 2.5×10^{13} photons/cm²-sec. and B would be down also by about 3 orders of magnitude. The importance of a high energy threshold for optical damage is obvious.

The time dependence of $\Delta\alpha_s$ can be analyzed by determining the time rate of change of k_i . Recalling that $k_i(\omega) = A_i F_i N_i / 2n_i$ and designating the term $A_i F_i / 2n_i$ by s_i , we can rewrite Eq. 34:

$$\Delta\alpha_s = \frac{1}{S} \int_0^\infty R_o(\omega) S(\omega) d\omega - \frac{1}{S} \int_0^\infty R_o(\omega) S(\omega) \exp\left[-a_i^{\frac{\gamma}{I}} s_i N_i(t)\right] d\omega \quad (36)$$

$$= R_s - \frac{1}{S} \int_0^\infty R_o(\omega) S(\omega) \exp\left[-a_i^{\frac{\gamma}{I}} s_i N_i(t)\right] d\omega, \quad (36a)$$

$$\text{where } R_S = \frac{1}{S} \int_0^{\infty} R_O(\omega) S(\omega) d\omega$$

It is easy to verify that $\Delta\alpha_s$ is zero when N_i is zero. Now, if the exponential term has very little or no frequency dependence, at least over the spectral range in which the defect(s) absorb, then it may be taken out of the integral such that

$$\Delta\alpha_s = R_S (1 - \exp[-a_i S_i N_i(t)]) \quad (37)$$

Differentiating Eq. 35 and substituting $k_i(\omega) = A_i F_i N_i$ leads to the expression

$$\frac{d\alpha_s}{dt} = \frac{1}{S} \int_0^{\infty} R_O(\omega) S(\omega) \cdot \exp[-a_i A_i F_i N_i(t)] a_i \sum_i A_i F_i \frac{dN_i(t)}{dt} d\omega \quad (38)$$

The degradation rate according to Eq. 38 decreases exponentially with time, the greatest rate being at time zero when $N_i(t)$ is zero. In very simplified form the instantaneous degradation rate is

$$\frac{d\alpha_s}{dt} = a_1 e^{-a_2 N} \frac{dN}{dt} \quad (39)$$

Time- and frequency-dependent terms can be separated provided that, in the summation of contributions from each i^{th} type defect, the summation sequence remains as required by Eq. 36a, i.e., first with respect to frequency.

D. The Kinetics of Solar Absorptance Changes

The quantity in brackets in Eq. 38 may, to first order, be regarded as a constant (i.e., independent of time). Hence, the rate of change of α_s is linearly related to the net rate of defect production, - a rate which itself may be exponential. Assume now that a single defect (e.g., an F center) is forming at the rate dN_F/dt . (The F center is an electron trapped at an anion vacancy.) If the irradiation does not affect the number density of anion

vacancies, the material will have (by assumption) an initial density of anion vacancies, N_v . The irradiation will generate free electrons, and some of these will be trapped by these vacancies. If the resulting F centers are stable, then they will appear at a rate:

$$\frac{dN_F}{dt} = B(N_v - N_F). \quad (40)$$

The factor B depends on irradiation rate, quantum efficiency, and the cross-section of anion vacancies for photoelectrons. Integrating Eq. 40 results in the expression:

$$N_F = N_v (1 - e^{-Bt}), \quad (41)$$

which is a simple first order kinetics relationship. In differential form it is:

$$\frac{dN_F}{dt} = BN_v e^{-Bt} \quad (42)$$

Finally, the expression for the time rate of change of solar absorptance due to the creation of a concentration N_F of one type of a stable absorption center becomes:

$$\frac{d\alpha_s}{dt} = \left[\frac{1}{S} \int_0^{\infty} R_o(\omega) S(\omega) e^{-ak_F^i N_F} ak_F^i d\omega \right] BN_v e^{-Bt} \quad (43)$$

Rewriting Eq. 43, and taking logarithms, the reciprocity law can be obtained, thus:

$$\begin{aligned} \log \Delta \alpha_s = \log & \left[\frac{1}{S} \int_0^{\infty} R_o(\omega) S(\omega) ak_F^i(\omega) e^{-ak_F^i(\omega) N_F(t)} \cdot d\omega \right] \\ & + \log BN_v \Delta t - Bt \end{aligned} \quad (44)$$

We can neglect $\log(BN_v \Delta t)$ and, at low exposures, the exponential term, obtaining a short form of the reciprocity law:

$$\log \Delta \alpha_s = -C_1 - Bt, \quad (45)$$

where

$$C_1 = \log \left[\frac{1}{S} \int_0^{\infty} R_o(\omega) S(\omega) a k_F^1(\omega) e^{-a k_F^1(\omega) N_F(t)} \cdot d\omega \right],$$

and this, except for the sign convention*, is exactly the form of the reciprocity law commonly found experimentally.

The failure of the usual reciprocity law (Eq. 45) at $t = 0$ and at $t = \infty$ is not evident in Eq. 44 because the term, whose log is designated as C_1 , would be approximately zero at time $t = 0$; hence its log would be $-\infty$ and $\Delta \alpha_s$ would properly be predicted as zero. The expression (Eq. 44) is not preferred as a prediction of solar absorptance degradation; it does, however, give some insight into the failure of most prediction schemes based on extrapolations of $\log \Delta \alpha_s$ vs exposure. At very high exposure levels the $\log BN_v \Delta t$ term can become important. Also, the C_1 term is really not a constant initially, because of the factor $N_F(t)$, consequently it has an effect on the manner in which $\Delta \alpha_s$ approaches to an asymptotic limit. Still another reason for reciprocity failures is the fact that a second defect type whose rate constant is B^1 ($B^1 \ll B$) may become important at times later than those associated with the first.

A more accurate prediction scheme comes from the log of Eq. 34a

$$\log \Delta \alpha_s = \log \left[\frac{1}{S} \int_0^{\infty} R_o(\omega) S(\omega) d\omega \right] + \log \left[1 - \exp(-a \sum_i k_i(\omega)) \right] \quad (46)$$

* The log of the quantity in brackets in Eq. 44) will be a negative number, hence, the negative sign in Eq. 45.

One should note that this prediction scheme involving $\log \Delta\alpha_s$ does not fail at time $t = 0$ ($k_i = 0$), because the right side of Eq. 46 equals $-\infty$, which is the anti-log of zero. At times approaching infinity $\Delta\alpha_s$ approaches the initial solar reflectance (the first term in Eq. 46).

In the case in which a defect is not stable, but is bleached by the radiation it absorbs, the kinetics expression becomes:

$$\frac{dN_F}{dt} = B(N_i - N_F) - B_b N_F \quad (47)$$

whose solution is:

$$N_F(t) = \frac{BN_i}{B + B_b} \left[1 - e^{-(B + B_b)t} \right] \quad (47a)$$

One can readily verify that bleaching has no effect on the form of Eq. 44, except to substitute $B + B_b$ for B . One important point to note here, however, is that the quantity $B/(B + B_b)$ depends upon the intensities of two different portions of the irradiation spectrum. Obviously, if the ratio of defect-producing to defect-bleaching intensities is not a constant, then the kinetics will not follow Eq. 47a, and may not even be reproducible.

A case which should be equally illuminating is that of a two defect system in which there is an interaction. The case in which there is no interaction is trivial and merely a complication in the preceding cases. Similar to the above cases, let there be a defect of Type 1 with the kinetics:

$$\frac{dN_1}{dt} = B_1(N_1^0 - N_1) - B_{b,1}N_1 \quad (48)$$

The second defect (Type 2) follows the kinetics:

$$\frac{dN_2}{dt} = B_2(N_2^0 - N_2) - B_{b,2}N_2 + B_{b,1}N_1 \quad (48a)$$

The interaction is such that Type 1 defects bleach to form a Type 2 defect which is also formed in an independent way and also bleaches.

The appropriate expressions are:

$$N_1(t) = \frac{B_1 N_1^0 (1 - e^{-B_1' t})}{B_1'} \quad (49)$$

$$N_2(t) = \frac{B_2 N_2^0}{B_2'} \left[1 - e^{-B_2' t} \right] + \frac{B_{b,1}^2 N_1^0}{B_1'} \cdot \left[\frac{1}{B_1' - B_2'} (e^{-B_2' t} - e^{-B_1' t}) \right] \quad (49a)$$

where $B' = B + B_b$,

The derivatives are:

$$\frac{dN_1}{dt} = B_1 N_1^0 e^{-B_1' t}, \quad (50)$$

and

$$\frac{dN_2}{dt} = B_2 N_2^0 e^{-B_2' t} + \frac{B_{b,1}^2 N_1^0}{B_1' (B_1' - B_2')} (B_1' e^{-B_1' t} - B_2' e^{-B_2' t}) \quad (50a)$$

It is not necessary to insert these derivatives into Eq. 38, since it is evident that the results are qualitatively the same as those obtained above. The log of the derivative in Eq. 50 gives the same form as in the F center example, and, if dN_1/dt is the controlling (most significant) defect, then the interaction is not important. If N_2 is the most important, then the log of dN_2/dt will also have the same form, provided that

$$B_1 \exp(-B_1' t) \ll B_2 \exp(-B_2' t).$$

A more complicated but yet common case arises when the kinetics are second order with respect to defect formation. Here the rate depends on the square of the net concentration of potential defects:

$$\frac{dN_F}{dt} = B(N_v - N_F)^2 \quad (51)$$

Second order kinetics result when two irradiation-produced precursor defects must combine to form a third. The concentration, N_F , of which depends upon the concentrations of the precursors. Thus in more general terms Eq. 51 should be written

$$\frac{dN_F}{dt} = B(N_A^0 - N_A)(N_B^0 - N_B), \quad (52)$$

where N_A and N_B are the precursor defects, and the superscripts indicate initial concentrations of their own precursors.

For the sake of simplicity, we will work with Eq. 51, the assumptions being that N_A and N_B are formed at the same rate and that they have negligible initial concentrations. Integrating Eq. 51, assuming N_F to be zero at time $t = 0$, gives the solution:

$$N_F = N_V^2 Bt / (1 + N_V Bt) \quad (53)$$

For reciprocity to be realized, it is necessary that N_F depend only on the product of intensity and time, and not on either individually. Provided that N_V remains a constant and is itself not a function of intensity or time, degradation involving second order kinetics will also display reciprocity.

E. Concluding Remarks

The conditions under which reciprocity will not be realized include irradiation at different sample temperatures, irradiation with different intensity ratios of two or more damaging radiations or of damaging/bleaching radiations. If the ratio of simulated solar wind flux to simulated solar ultraviolet intensity differs from that existing in the space environment, a question of simulation will arise, and reciprocity is unlikely if the ratios are not the same from one test to another. This does not mean, however, that irradiation rates can not be accelerated. Accelerated rates will endanger reciprocity and simulation as sample temperatures increase as a result of higher irradiation rates. Annealing, for example, a process the rate of which depends

only on temperature, can cause serious discrepancies in tests conducted at different irradiation rates.

The degradation of solar absorptance, with a reasonable knowledge of materials properties and environment parameters, can be predicted through kinetics models such as those developed in this section. Though they are somewhat complex, they represent major advances over the reciprocity law commonly used to predict or correlate solar absorptance degradations. These models, furthermore, should be very useful in interpreting and understanding the effects of the real and the simulated space environment.

V. MATERIALS AND MATERIALS CHARACTERIZATION

A. Basic Objectives

The prime objective in the experimental studies was to determine the role of particle size in initial reflectance and in optical stability - with emphasis on the former. As it turns out, particle size is a very elusive quantity; it is a description which has many derivations and many interpretations. Particle size is related to surface area; and surface activity, to surface area. Depending on the material, particle size may have an inherent limit, one arising from the resistance of surface forces to further subdivision and the complementary tendency to re-associate. Therefore when particles are made microscopically small, they tend to re-associate - to aggregate into larger "chunks." To distinguish the optical (spectral reflectance) effects which are due to particle size (d_p) alone, those which are due to their aggregates (d_A), and those due to the voids between them (d_v) is thus a major objective.

The effects of these variables on initial reflectance and particularly on reflectance stability can only be ascertained if the physical characterizations can be made successfully. Initial reflectance properties can be compared only when the materials have the same physical characterizations. The effects of these parameters on stability can be determined only if both the physical and chemical characterizations of the material are the same. Thus we have as an intermediate objective that the materials be as chemically identical as possible - that they differ in particle size and only in particle size.

B. Pigment Materials - Criteria and Selections

The four pigments selected for study in this program were Alumina (Al_2O_3), Silica (SiO_2), Zirconia (ZrO_2) and, by contractual specification, Lanthana (La_2O_3). The first two were selected mainly because of their extensive literature backgrounds and their potential use as thermal control pigments. Each also has been

widely used in commercial coatings. Zirconia was chosen because of its potential stability to ultraviolet radiation. The resistance of La_2O_3 to the effects of protons and its poor ultraviolet behavior prompted its choice. Other materials were also used - mainly zinc sulfide (ZnS) - because of special absorption properties which could be used to demonstrate the effects of scattering. Semiconductor pigments (e.g., ZnO and TiO_2) were excluded from consideration, since the ultimate objective is a low α_s/ϵ paint pigment. Organic materials, except test vehicles, were also excluded.

In the initial stages of the program, we hoped to obtain pigment materials available in several sizes and in size distributions with particles as monosized as possible in the size range from 0.1μ to 10μ .

Additionally, and most importantly, we required that the only difference between the various particle sizes of a given material be particle size itself.

Efforts to obtain sample materials were made mainly by telephone and letter contacts. Our intention was to acquire pigments in the range 0.1 - 10.0μ , and hopefully as many as five "sub-size" ranges within this range. The requirement that the only difference between these materials must be size itself along with the other requirements greatly reduced the number of potential suppliers. Numerous suppliers whose names were screened from The Thomas Register, trade journals and materials catalogs were contacted; some supplied samples, others gave leads on other suppliers.

A large number of companies manufacture, beneficiate or supply powders, paint pigments and other finely divided solid materials, but few supply those of interest here. In communications with these companies, we outlined our requirements and attempted to discern for each of their products the particle size(s) and range(s), the purity and chemical composition of each, the availability of certified chemical analyses, and cost information. In the following list are the companies contacted, the products of interest (in parentheses), and their response, if any.

Table 1
LIST OF PIGMENT SOURCES

1. Malvern Minerals Co. (SiO_2)
Hotsprings National Park, ²Ark.
Samples of and literature on altered Novaculite.
2. Degussa, Inc. (SiO_2 , Al_2O_3 , ZrO_2 , La_2O_3)
New York, New York²
No reply
3. Potters Bros., Inc. (Silica glass spheres)
Carlstadt, New Jersey
Too large, range in size from 44-840 microns
4. Harshaw Chemical Co. (Al_2O_3 , SiO_2 , ZrO_2 , La_2O_3)
Hinsdale, Illinois
Negative on all materials.⁺
5. Allied Chemical Co. (Al_2O_3)
Industrial Chemicals Div.³
Chicago, Illinois
Negative
6. Reynolds Metals Co. (Al_2O_3)
Chicago, Illinois
Negative
7. Aluminum Corp. of America (Al_2O_3)
Chicago, Illinois
Samples of Hydral 705, 710 and 710S (aluminum hydrates).
- *8. TAM - Division of National Lead (Al_2O_3 , SiO_2 , ZrO_2 , La_2O_3)
New York, New York
Can supply ZrO_2 in less than 10 micron size, but cannot separate into particle size ranges. Cost - \$11.00/lb.
9. Kaiser Chemicals (Al_2O_3)
Div. of Kaiser Aluminum
Chicago, Illinois
Sample of and literature on hydrate (KH-31 fines)

⁺ Negative means that the company could not meet one or more of our requirements, e.g., particle size <10 microns, max.

Table 1 (Cont'd)

10. TAM - Division of National Lead (Al_2O_3 , SiO_2 , ZrO_2 , La_2O_3)
Research Department
Niagara Falls, New York.
Same reply as in No. 8.
- *11. American Potash and Chemical Co. (La_2O_3)
West Chicago, Illinois
 La_2O_3 code 529.9 (99.999% pure), 0.1-1.0-micron size,
\$225.00/lb. Less pure grades, codes 529 and 528, also
ordered.
12. Pfizer Chemical Co. (Al_2O_3 , SiO_2 , ZrO_2 , La_2O_3)
Minerals, Pigment and Metals Div.
Chicago, Illinois
Negative
13. Davison Chemical Co. (Al_2O_3 , SiO_2 , ZrO_2 , La_2O_3)
Division of Grace Chemical Co.
Negative
14. Michigan Chemical Co. (Al_2O_3 , SiO_2 , ZrO_2 , La_2O_3)
Chicago, Illinois
Negative
15. Illinois Minerals Co. (SiO_2)
Cairo, Illinois
Samples of and literature on "Imsils"
16. K.C. Abrasives Co. Precision separators
Kansas City, Mo.
Do not have capabilities for separating particles in the
submicron size range.
17. Chicago Vitreous Corp. (Al_2O_3 , SiO_2 , ZrO_2 , La_2O_3)
Div. of Eagle Picher Co.
Cicero, Illinois
Negative
18. International Minerals & Chemicals Corp. (SiO_2)
Industrial Minerals Div.
Skokie, Illinois
Negative

Table 1 (Cont'd)

19. American Graded Sand Co. (SiO_2)
Div. of Ottawa Silica Co.
Des Plaines, Illinois
Negative
20. Norton Co. (ZrO_2)
Des Plaines, Illinois
900 mesh (11-micron size) \$3.00/lb.

21. Crystal Optics (SiO_2)
Chicago, Illinois
Negative

- *22. Linde Crystal Products (Al_2O_3)
Div. of Union Carbide
East Chicago, Indiana
Dry powders used as optical abrasives (99.9+% pure).

<u>Grade</u>	<u>Form</u>	<u>Particle Size (μ)</u>	<u>Cost/lb</u>
*A	Alpha	0.3	\$20.00
B	Gamma	0.05	20.00
*C	Alpha	1.0	20.00

- *23. Cabot Corp. (Fumed SiO_2 and Al_2O_3)
Oak Brook, Illinois

Fumed SiO_2

<u>Grade</u>	<u>Particle Size (μ)</u>	<u>Cost/lb</u>
EH5	0.007	\$ 1.42
M5	0.012	1.25
*L5	0.05	1.95

Fumed Al_2O_3

Alon	0.03	1.95
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Samples and literature received.

- *24. Adolf Meller Co. (Al_2O_3)⁺⁺
Providence, Rhode, Island
Alumina in particle sizes: *0.06, *0.3 and *1.0 μ (\$12.00/lb);
*3.0 and 8.0 (\$15.00/lb)

*The asterisks in the left margin indicate those companies from whom we obtained the final selection of materials and the other asterisks as appropriate, the actual materials ordered.

++The Authors acknowledge and appreciate the assistance of Mr. Carl P. Boebel of the Air Force Materials Laboratory (MANE) and of Mr. Gary Stevenson of the Univ. of Dayton Research Institute, who suggested the Meller Co. as a source of graded sizes of Alumina pigments.

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Consideration was also given to possible direct production techniques, e.g., calcination, vapor deposition, solution growth, the Bell Telephone "cryo" method; and also to classification techniques such as the Barco Centrifuge and aqueous settling. After reviewing these possibilities we concluded that because of cost and schedule considerations, we would first exhaust all potential commercial sources. Currently available techniques for size separation in the submicron range are very limited in both the size ranges they can work with, and especially in production rates (quantities of grams/day). In the submicron range, the best that can be done is to separate the particles smaller than a pre-selected size in a given sample from larger ones. It is not possible to fractionate out a narrow range, say $0.2\text{--}0.3\mu$, from a sample whose size distribution ranges from, say, 0.05 to 2.0μ .

As for the direct production methods, cost, impurity control, and consistent physical properties become important. Costs alone are substantial because the optimum operating conditions in the production apparatus are not known a-priori, and determining them becomes a sizeable research task. In some of these techniques, particle shape, chemical purity, and crystal habit vary with particle size; chemical purity, for example, is often a strong function of the operating conditions which must be varied to generate different particle sizes; this is especially true in hydrothermal techniques.

C. Materials Characterization Techniques

1. General Remarks

Terminology may become a difficult barrier in a research program such as this one. We therefore believe that it is highly important to define terminology to avoid confusion. Particle size, for example, can be understood in many different ways, and, unless criteria for determining size are clearly stated, it is most likely to be misunderstood. The terms particle, aggregate and agglomerate are very frequently used. The term particle,

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however, is usually qualified by one of the words: single or discrete. The meanings are identical and imply that the particle is a single mechanical entity and that it does not display any obvious signs of further subdivision. The term single particle carries with it the meaning that the particle acts as an individual particle; and discrete particle, that the particle is clearly evidenced as an individual object unassociated with and not composed of others. In speaking of particle size, the term ultimate particle size is used to distinguish the size of a particular particle which may obviously be associated with others from that which might be attributed to it if it were a discrete particle, although there is the presumption that the discrete particle size may be deduced from its apparent size in an aggregate. Referring to our photomicrographic measurements, size in every case is an average length value corresponding to the longer of two planar coordinate dimensions; in the case of a sphere, it is the diameter; and in cubic materials, it is the length of a side. Shapes vary so greatly in some materials that their size measurements can not really be regarded as objective when only one size value is cited.

Depending on what measurement techniques are employed, "size" may range over more than an order of magnitude; the size of a porous particle when optically determined will be much greater than that determined by BET. Size analysis is an extremely difficult problem, when porous, non-spherical particles are being measured. The true size can almost become subjective depending upon the technique(s) used to measure it and the property really intended to be measured. This will be discussed in greater length in the next section.

An agglomerate and an aggregate are essentially the same thing - a conglomeration of single particles held together by mutual attraction, Van der Waal forces, etc. A distinction is made between the two in that the term aggregate applies to any multi-particle mass whose formation history is unknown. An agglomerate is an aggregate formed by aggregation of discrete

particles and/or smaller aggregates under the influence of electrostatic forces, mechanical dispersion, evaporation of the media in which they existed, or similar external forces tending to bring them in contact. These terms, of course, also refer to processes and they thus have action meanings, which are likewise distinguished. The process of aggregation refers to any previous and thus unknown process which forms an aggregation of single particles. Agglomeration is simply the process of forming an agglomerate. These distinctions even though subjective are helpful in size characterization. In an "as-received" sample, for instance, there will be some material in an aggregated form, and the remainder in the form of discrete particles. Since we do not know what produced the former, we simply call them aggregates. After ball milling or dispersing the "as-received" sample, the proportions of aggregates and fines may be entirely different, and if the aggregate count is increased substantially, we call them agglomerates.

Particle shape probably has the most subjective definition of any of the terms we will use. In general, the term shape refers to a three dimensional geometrical description of a particle or an aggregate. The subjectiveness enters into the definition through the interpretation of the various measurements which can be made. Optical determinations, the most direct, are two-dimensional; other techniques measure shape-related quantities but not shape itself. In this report we determine shape primarily on the basis of scanning and transmission electron microscope photomicrographs. Thus we rely mainly on the statistics of many particles and aggregates and assume that they are randomly oriented such that all facets of any particular type of particle will be seen in the photomicrographs. For example, if a particular type of particle has 10 faces, 5 of which were different from one another, the probability that all 5 faces would be seen in a photomicrograph would be better than 50% if there were more than 5 particles. If there were 1000+ particles in the field of view, this probability would be essentially 100%. For further

discussions of particle shape and its effect on reflectance, the reader is referred to Ref. 29.

Particle geometry, another term frequently used in this report, is the composite of size and shape. It refers to the full quantitative three-dimensional characterization. The term film structure refers to the physical and geometrical arrangements of particles and agglomerates relative to one another in a deposited film, and it is in this context that particle geometry has a recognizable meaning. The space in a paint film between the particles and the agglomerates which is not occupied by solid matter is a void. The term void structure means the physical and geometrical configuration of the voids relative to one another. In a foamed material for example, void structure would be the physical and geometrical distributions of air bubbles.

Lastly, it is well to distinguish the dimensional levels implied in the above remarks. Since we are dealing with the solar spectrum, the wavelengths, of interest are 2000 - 30,000 nm ($0.2 - 3.0\mu$); and, assuming a factor of 10 in the ratio of d_p/λ to be important, the range of characteristic particle dimensions from 0.02μ to 30μ becomes the range of primary interest, from the dimensions of the smallest discrete particle to those of larger aggregates.

2. Size Analysis

Using a centrifugal disc photo-sedimentometer the Stokes' diameter distribution of a powder may be determined over the size range 10 to 0.1μ . The Stoke's diameter of a particle is the diameter of the sphere of equal density to the particle having the same settling velocity as the particle. Thus the true diameter and the Stokes' diameter of a flake is smaller than the projected diameter. The measurement is made by sedimentation through a liquid in a centrifuge. Detection relies upon optical scattering. Unlike the centrifugal method of sizing, an electron microscope provides data on the projected area of each particle,

gives an indication of shape and in the 10 to 0.1μ range measures the true dimensions. Transmission electron microscope (TEM) photomicrographs can be obtained at magnifications up to 85,000X and these can be used to measure size distribution and a projected area, and to quantify shape. Shadowing techniques are used to estimate particle thickness.

The surface area of powders accessible to nitrogen gas may be measured by static (BET) or dynamic gas absorption techniques. The measurement is of total surface area and includes that attributed to surface texture and internal porosity. In this technique nitrogen gas is adsorbed onto the powder surfaces at liquid nitrogen temperature. The quantity of gas adsorbed is determined by pressure measurement. The nitrogen deficiency may be related to the total surface area of the powder from which an effective particle size (spherical) may be estimated (Ref. 30).

The outside or wetted surface area of a powder may be determined by a permeability technique in which a gas, such as air, is flowed through a packed bed of the powder. Pressure differential and flow rate measurements are made and used to calculate the external surface area.

Apart from the direct measurement of Stokes' diameter distribution, projected area distribution, and total and external surface areas described above, comparison of data yields additional information. The ratio of Stokes' median diameter to projected median diameter, for example, is a shape factor. In the case of spherical particles the factor is one, but departs rapidly from this as the shape becomes more extreme. The shape factor is a mathematical means of describing the average shape of the irregular particles. This factor complements and quantifies the usual display of shape given by the TEM. Again, the reader is referred to Ref. 29 for further discussions on particle shape and shape analysis.

The surface area for the Stokes' distribution may be calculated assuming the particles are smooth solid spheres. Comparison of this with the external surface area measured by permeametry yields a mathematical description of surface roughness.

The difference between the total and the external surface area is a measure of the internal surface and hence a measure of void structure within individual particles.

3. Particle Size and Shape Measurements

The main emphasis of this phase of work was to obtain information on the particle size and shape of the various coating materials. An Hitachi HS-6 transmission electron microscope was utilized in obtaining information on the sub-micron particles and a Zeiss optical microscope was used for the larger particles. The basic technique utilized with the TEM in determining particle size and shape was to prepare a suspension by dispersing ultrasonically for 5 min. a small amount of the sample material in water or alcohol. A small drop of the suspension was then placed on a coated electron microscope grid. Collodion, Formvar, or carbon was utilized as a coating material, the choice of which was made empirically.

For use with the optical microscope the sample material was placed on a glass slide and covered with a cover slip. With dry samples, a drop of dispersion media was used with the cover slip to obtain a representative slide. Prepared suspensions were directly utilized on a glass slide with cover slip. Photographs were taken to record the observations, and the data from those are summarized in Table 2. The description of particle shape is an arbitrary judgement of the observer and as such may differ from others. Representative photographs of the powder samples are presented for the reader's interpretation.

Although numerous transmission electron microscope photographs on glass slides were taken, they will not be shown

Table 2

PARTICLE SIZE AND SHAPE OF RAW MATERIALS

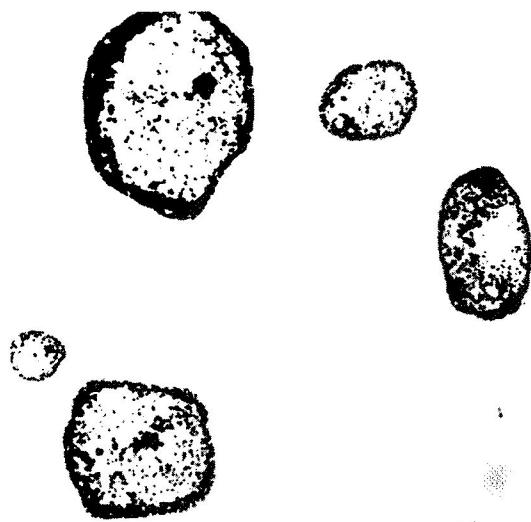
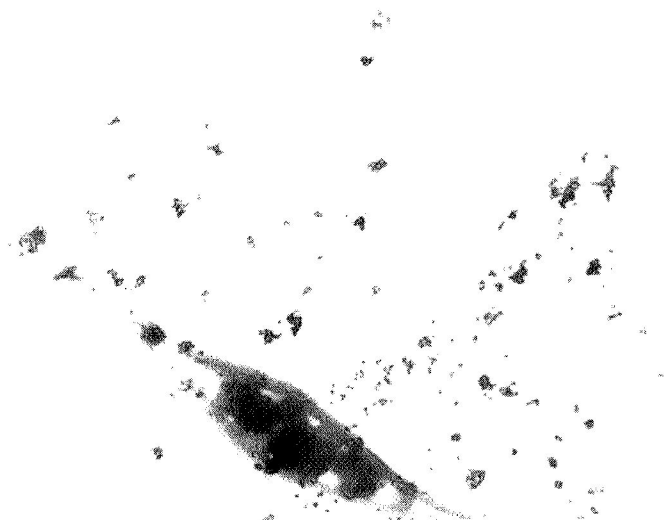
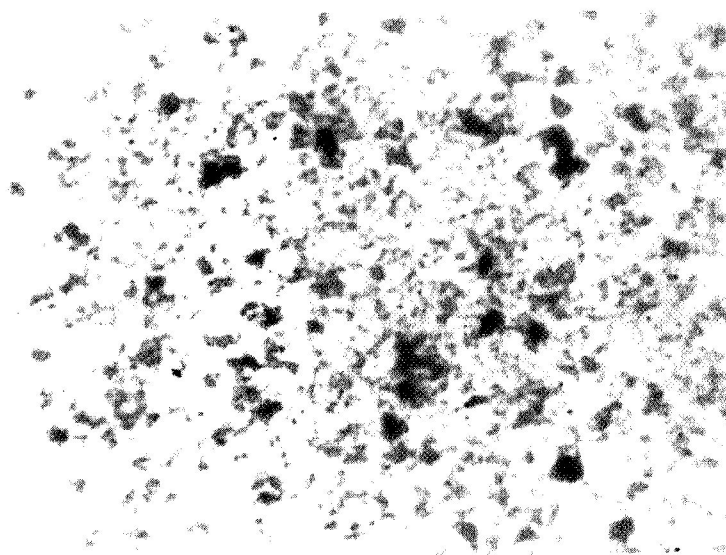
Pigments	Smallest Particle, μ	Largest Particle, μ	Average Size, μ	Shape
ZnS - No grinding	0.05	0.4	0.1-0.2	Near spherical
ZnS - 96 hr grinding	0.05	0.4	0.1-0.2	Near spherical
ZrO ₂ - 24 hr grinding	0.15	0.7	0.3-0.4	Irregular spheres
ZrO ₂ (Dispersed)	0.15	0.7	0.3-0.4	Irregular spheres
La ₂ O ₃ - 528	0.2	5.5	0.5-0.8	Irregular agglomerates
La ₂ O ₃ - 529	0.15	0.8	0.2-0.4	Irregular agglomerates
La ₂ O ₃ - 529.9 (Undispersed)	0.11	0.5	0.2-0.4	Irregular agglomerates
La ₂ O ₃ - 529.9 (Dispersed)	0.05	0.5	0.1-0.4	Irregular agglomerates
Cab-O-Sil L-5	(0.05)	(0.05)	(0.05)	(0.05 μ) Filaments
Alon-Cabot	(0.03)	(0.03)	(0.03)	(0.03 μ) Filaments
Linde A (Dispersed)	0.1	0.8	0.25-0.5	Fused curves
Linde C (Dispersed)	0.25	1.0	0.5-0.75	Fused curves
Meller's Alumina 0.06 μ	0.01	0.10	0.06	Agglomerated and small
Meller's Alumina 0.3 μ	0.05	0.3	0.2	Agglomerated and small
Meller's Alumina 1.0 μ	0.2	0.6	0.4	Agglomerated and small
Meller's Alumina 3.0 μ	0.2	0.8	0.5	Agglomerated and small

 () = Manufacturer's sizing data.

in this report, because of the difficulty of reproducing them, and because of the large number of them which must be observed in order to deduce size and shape information.

4. Spray Studies

As work progressed on particle characterization of the raw powder material, a short study was made on the spray process itself. In the spray process, the raw sample material must be fluidized; if it doesn't wet easily or at all, dispersion will have to be achieved through mechanical or chemical means. (In this project, we did not use chemical dispersing agents). After mechanical dispersion - ball milling, hand mixing, sonifying, etc., the suspension is sprayed onto a substrate. The point to these tests then was to determine the particle characterization at each step in order to determine how it changed and if the characterization of the particles in a binderless film bore any resemblance to that of the raw powder from which it was initially prepared. Under the microscope it is possible to watch the aggregation process during evaporation of the liquid media. As a drop becomes smaller and smaller, the discrete particles get closer together and eventually agglomerate. The size of the agglomerate depends upon the initial number of discrete particles and the number and size of aggregates initially in the drop. The raw powder was dispersed in the fluid media, water or alcohol, and sprayed on to a glass slide or on to the substrate material. The as-received powder, a sample of it in a solution to be sprayed, a sample of it caught mid-way between the spray gun and the target, and another sample of it caught just ahead of the substrate were examined in the TEM. The particle size of the raw powder, the degree of dispersion in the suspension, the spray droplet size, and the spray concentration were shown to be important factors in the structure of the final coating. Figures 4 and 5 are indicative of two factors in spraying: the presence of aggregates in the spray droplet which is comparatively large relative to powder particle size, and the drying or evaporation of fine



(a) Original Suspension (400X) (b) Suspension as it is drying under cover slip (400X) (c) Spray on glass slide (100X)

Figure 4. PHOTOGRAPHS OF ZrO_2 (24 HR GRIND) ON GLASS SLIDES



(a) Spray on Glass Slide (40X)



(b) Spray on Glass Slide (40X)

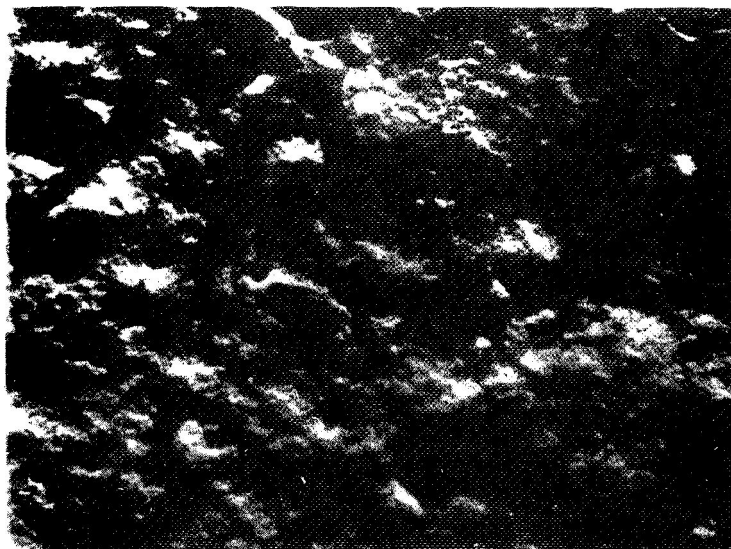
Figure 5. PHOTOGRAPHS OF LINDE A (a) AND LINDE C (b)
ON GLASS SLIDES

droplets prior to substrate deposition resulting in agglomerates depositing on the substrate. Spraying results in irregular or non-uniform surface as seen in Figure 6. Figure 4 is a sequence of photographs taken first of the original suspension, of ZrO_2 in water, then of the spray itself (shown under a cover glass to prevent further evaporation), and finally of the spray droplets on a glass slide substrate. Figure 5 compares photographs of suspensions of Linde A and Linde C sprayed onto glass slides; agglomeration is obviously very extensive. The process of wet-spraying obviously does not preserve the particle geometry characterization of the original material. To maintain the original characterization considerable thought must be given to the nature of the material and the technique. In these photographs, unless otherwise noted, the light angle on the sample is 10° above the sample plane (to enhance topography).

The effect of agglomeration in producing a rough surface, is shown in Figure 6 where two different light angles have been used. The coating is wet-sprayed ZrO_2 .

5. Deposition Studies

To understand the problem of irregular surface topography, a study was made of substrates formed by particles settling out of aqueous suspensions on a substrate. Two interdependent variables for consideration were the degree of dispersion of the suspension and the particle size distribution. Poor dispersion would result in the presence of agglomerates and a wide particle size distribution would result in a stratified type of deposit. Figure 7 illustrates, in the case of ZrO_2 , the difference in dispersion achieved by hand mixing (Figure 7a) and by an ultrasonic treatment (Figure 7b). Figure 8 indicates the type of film formed from two differing particle size distributions: Linde C (nominally 1.0μ) vs Linde A (nominally 0.3μ). Compared to spray coatings these surfaces are very smooth, and the Linde A surface appears to be smoother than that of the Linde C.

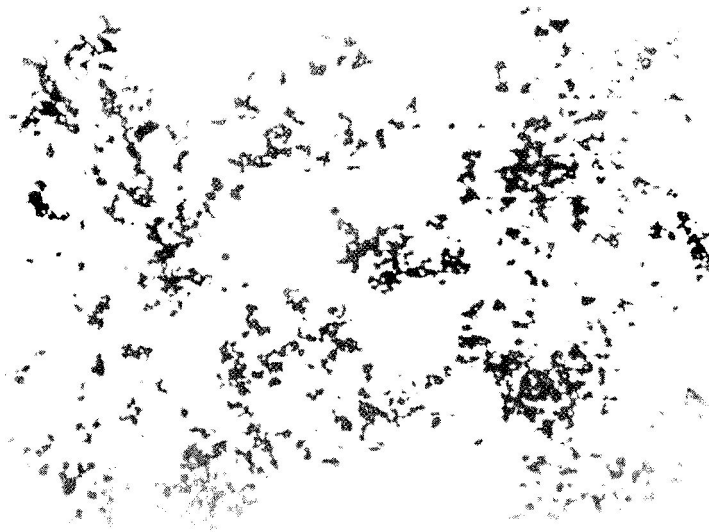


(a) Deposit on Coupon (40X)
Illuminating 10° Light Angle

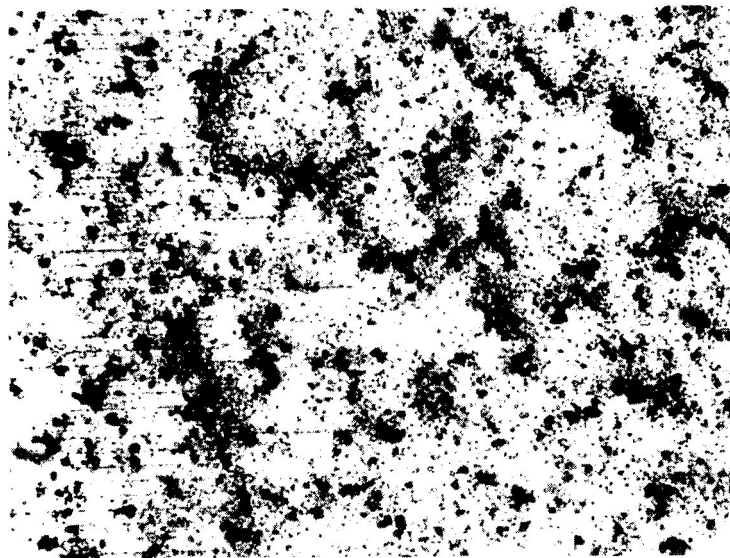


(b) Deposit on Coupon (40X)
Illuminating 45° Light Angle

Figure 6 PHOTOGRAPHS OF A ZrO_2 BINDERLESS FILM (24 HR GRIND)
AT LIGHT ANGLES OF 10° AND 45°

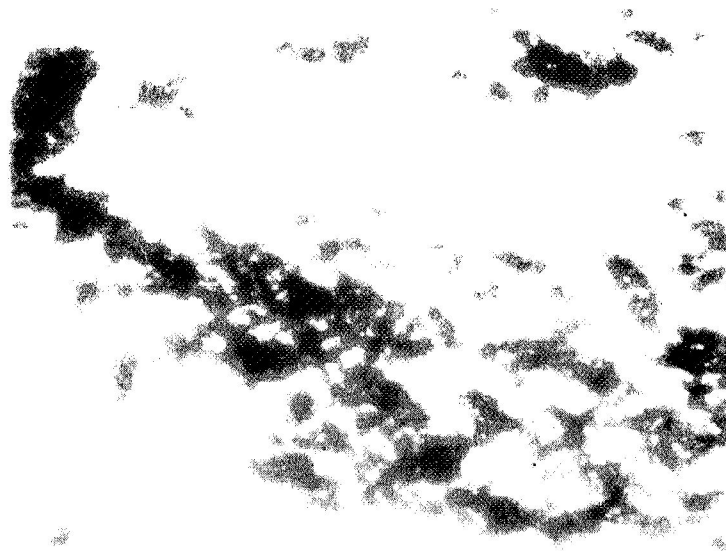


(a) Undispersed

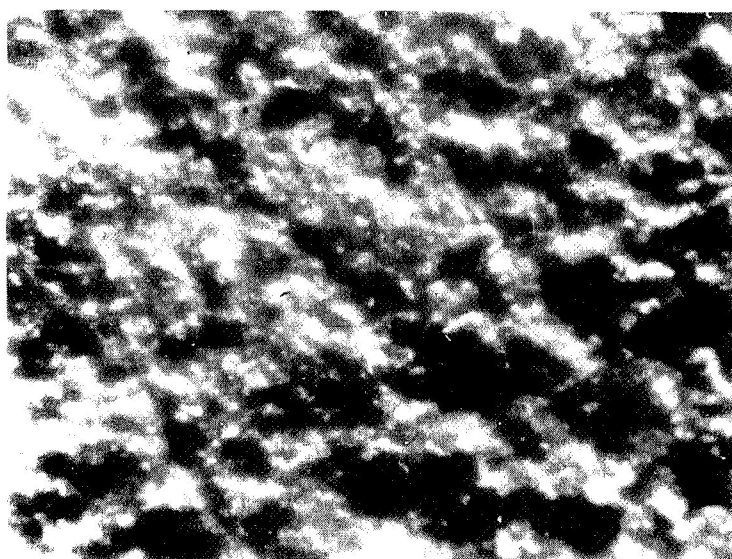


(b) Dispersed (Ultrasonically)

Figure 7. PHOTOGRAPHS OF ZrO_2 - UNDISPERSED VS. DISPERSED
(HORIZONTAL GRID LINES ARE 10μ APART)



(a) Film Deposit from Settling (40X)
Illuminating 10° Light Angle



(b) Film Deposit from Settling (40X)
Illuminating 10° Light Angle

Figure 8. PHOTOGRAPHS OF LINDE C (a) AND LINDE A (b)
BINDERLESS FILM FORMED BY SETTLING FROM
AQUEOUS SUSPENSIONS

6. Surface Studies

A microscope study was made of a few surfaces formed by rapid filtration of undispersed and dispersed aqueous suspensions of Linde A, Linde C and ZnS. The filtration process minimized stratification effects which differences in sedimentation or settling rate might otherwise have caused. The results as seen in Figure 9 show that a more closely sized powder material results in a more uniform surface. The zinc sulfide coating, especially, shows a very dramatic increase in smoothness with dispersion.

7. Surface Area

Surface area measurements were made on Linde A and Linde C alumina with the BET apparatus, the basic technique for which is described in Ref. 26. The results are tabulated below.

<u>Material</u>	<u>Area (B.E.T.)</u>	<u>Surface Mean Diameter*</u>
Linde, Type A Al_2O_3 (0.3μ)	9.18 m^2/g	0.164 μ **
Linde, Type C Al_2O_3 (1.0μ)	3.07 m^2/g	0.49 μ ***

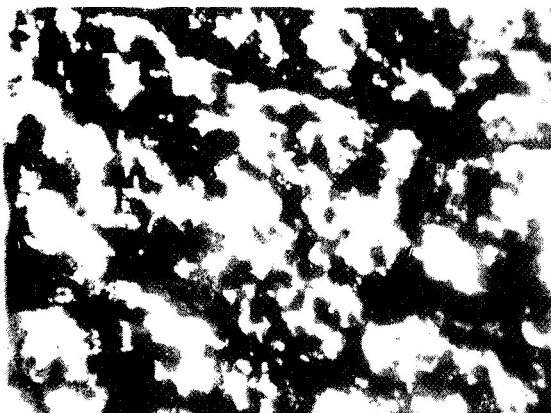
*Diameter of monosized alumina (assuming a spherical shape, and a density of 3.99 gm/cm^3) that will have the measured surface area.

**Manufacturer claims diameter is 0.3μ .

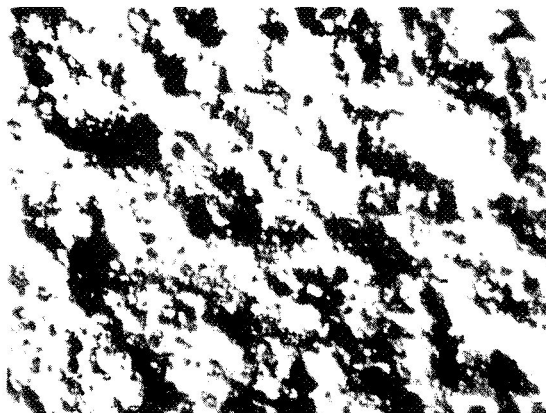
***Manufacturer claims diameter is 1.0μ .

8. Porosimetry

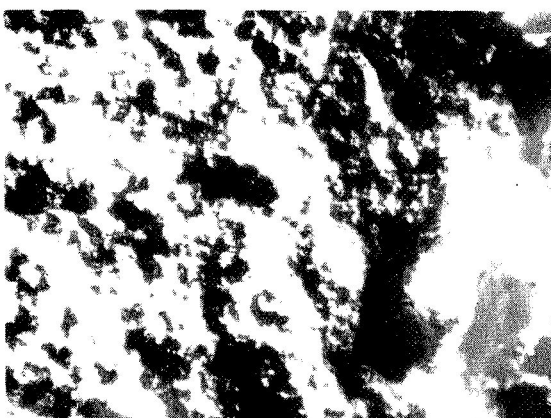
The Aminco-Winslow Mercury Porosimeter was utilized to obtain Pore Size distribution of Linde A and Linde C alumina powder samples. In this method, the sample is placed in a graduated penetrometer and the system evacuated. Mercury is introduced under increasing pressure. As the mercury is forced into the sub-micron pores of the sample, capillary stem readings on the penetrometer are recorded manually. These data: capillary stem readings (pore volume) and pressure (pore diameter) are plotted on special 5-cycle semi-log graph paper with pore volume on the vertical



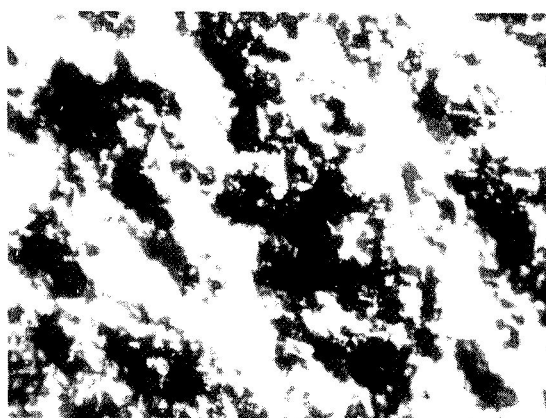
(a) Linde A - Undispersed (40X)



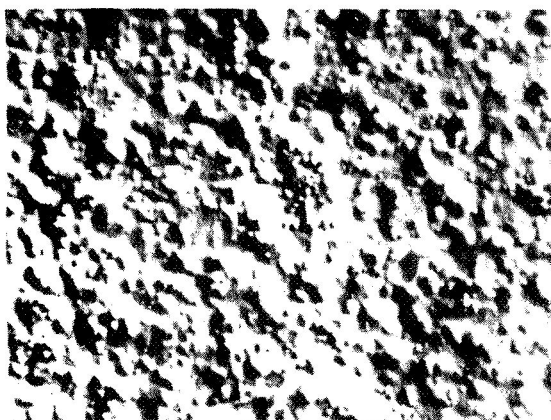
(b) Linde A - Dispersed (40X)



(c) Linde C - Undispersed (40X)



(d) Linde C - Dispersed (40X)



(e) ZnS - Undispersed (40X)



(f) ZnS - Dispersed (40X)

Figure 9. PHOTOGRAPHS OF LINDE A, LINDE C AND ZINC SULFIDE BINDERLESS FILMS FORMED BY SETTLING FROM AQUEOUS SUSPENSIONS - UNDISPERSED VS. DISPERSED

axis vs. pore diameter on the logarithmic horizontal axis. The particular model of instrument used has a capacity of 3000 psi and provides data on void size (100 to 0.05 μ), void size distribution, and total volume of pores.

Attempts were made to utilize this method with compacted coatings. It was found that a binderless coating material as prepared could not be utilized with the porosimeter. The original powder prior to use as a coating, however, could be characterized in this way.

9. Scanning Electron Microscopy

The Jeolco, (Japan Electron Optics Corp.), scanning electron microscope (SEM) Type JSM-2 was utilized for a more highly magnified, direct study of the surface of binderless films. This instrument has a resolving power of 250 Angstrom Units (A.U.) and a magnification range of 45X - 80,000X.

The sample deposits were placed on a special steel substrate material. Being non-conductive they were first coated with a thin film of gold in a vacuum evaporator. Photographs at various magnifications were taken at selected microscopic sites. The SEM photomicrographs show both the individual particles and the agglomerates that make up the total arrangement of the surface. A visual comparative examination of the various samples has shown that the use of ultrasonically dispersed material in the preparation of the deposit results in a more uniform surface and that the smaller size materials exhibit a tighter and more orderly packing arrangement. The results of a comparison of two different alumina samples appear in Table 3.

D. Materials' Characterization Procedure

A methodical and routine procedure was followed in the characterization process. Each material received was examined in a transmission electron microscope (TEM). To get reasonable statistics we usually examined a minimum of 1000 particles.

Table 3

MEASURE OF POROSITY FROM SCANNING ELECTRON MICROSCOPE PHOTOMICROGRAPHS

I. Meller's Alumina, 1.0 μ sample

Photomicrograph #219 (undispersed) 300X (Figure 38)

Photomicrograph #228 (dispersed) 300X (Figure 85)

	Undispersed	Dispersed
Total number of aggregates*	61	173
Total number of voids	34	125
Smallest aggregate	$6\mu \times 10\mu = 60\mu^2$	$3\mu \times 3\mu = 9\mu^2$
Largest aggregate	$40\mu \times 60\mu = 2400\mu^2$	$35\mu \times 40\mu = 1400\mu^2$
Approximate Size Distribution of Aggregates		
60 - $460\mu^2$	35	63
460 - $960\mu^2$	20	7
960 - $1460\mu^2$	3	3
1460 - $2060\mu^2$	2	0
2060 - $2400\mu^2$	<u>1</u>	<u>0</u>
Total	61	173
Approximate total area of voids		
	$3500\mu^2$	$1400\mu^2$
Smallest void	$3\mu \times 3\mu = 9\mu^2$	$2\mu \times 2\mu = 4\mu^2$
Largest void	$30\mu \times 50\mu = 1500\mu^2$	$12\mu \times 10\mu^2$
Per Cent Porosity**	8.75%	3.4%

II. Linde A Alumina (nominally 0.3 μ)

Micrograph #238 (undispersed) 300X (Figure 75)

Micrograph #231 (dispersed) 300X (Figure 76)

	Undispersed	Dispersed
Total number of aggregates*	110	400
Total number of voids	88	300
Smallest aggregate	$3\mu \times 3\mu = 9\mu^2$	$2\mu \times 2\mu = 4\mu^2$
Largest aggregate	$15\mu \times 50\mu = 750\mu^2$	$15\mu \times 20\mu = 300\mu^2$
Approximate Size Distribution of Aggregates		
9 - $209\mu^2$	78	385
209 - $409\mu^2$	20	15
409 - $609\mu^2$	8	0
609 - $809\mu^2$	<u>4</u>	<u>0</u>
Total	110	400
Approximate total area of voids		
	$2700\mu^2$	$500\mu^2$
Smallest void	$3\mu \times 3\mu = 9\mu^2$	$2\mu \times 2\mu = 4\mu^2$
Largest void	$20\mu \times 20\mu = 400\mu^2$	$10\mu \times 10\mu = 100\mu^2$
Per Cent Porosity**	6.75%	1.25%

*Photomicrographs are 6cm x 6cm; field of view, at 300X, corresponds to $200\mu \times 200\mu = 40,000\mu^2$.

**Estimated on an area basis.

Basically, in the TEM studies we looked for particle size and shape information. Materials which exhibited considerable particle size and shape variations were rejected. Thus, we used the TEM as a screening tool to narrow down the choice of materials.

Deposited films were characterized according to their weight and thickness. The film weights, in grams, were measured to the nearest 0.0001 gram. Since the substrates used are known to be flat and to have parallel faces within ± 0.0001 -in, the thicknesses of the deposits were determined by the difference in the height of an optical stage focussed first upon the substrate (a tiny corner of the film was scrapped off) and then on the coating. An average was taken over a minimum of 8 readings. The precision of this method is ± 0.0003 in. The accuracy, we believe, is at least ± 0.0005 in. The weight/thickness ratio, therefore, can be determined with very good precision and with more than adequate accuracy.

Spectral reflectance measurements in the range $0.22\text{-}2.6\mu$ ($2200\text{\AA}$ - $26000\text{\AA}$) were made using the Beckman Dk-2A spectrophotometer with an IITRI designed Edwards Sphere attachment. The reflectance spectra of all samples were obtained using this instrument. The spectral reflectances of all samples exposed to simulated solar radiation were also measured in-situ in IRIF-II. This system, described elsewhere (Ref. 37), incorporates an evacuable Edwards sphere optically connected to a Beckman Dk-1 spectrophotometer.

E. Sample Preparation - Reflectance Measurements

The majority of the samples prepared for reflectance measurements were in the form of binderless films on aluminum substrates. The advantages to this preparation technique are that the powder materials can be studied without contaminating them and without superimposing foreign characteristics on theirs, and that the resulting films have densities similar to those in highly pigmented paint systems. A disadvantage is that the PVC ratio can only be varied over a small range and thus achievable variations in

interparticle separations are very limited. But binderless films have the advantage that their reflectances are much higher than pigment-vehicle dry films because the effective refractive index of the "vehicle" (voids) in a binderless film is unity. The tedious calculations involving the optical constants of the vehicle over the spectral region of interest need not be carried out when binderless films can be studied.

The necessity for all samples of any given material to be as nearly the same in structure and thickness as possible made the preparation task a difficult one. Numerous techniques were tried in order to prepare such samples, but it was found that each material behaved differently and thin films were not easily reproduced.

Some materials, such as Meller's 0.06μ Al_2O_3 and Cabot Corp. Cab-O-Ti (TiO_2) and Cab-O-Sil L-5 (SiO_2) could not be applied successfully at all by any of the techniques tried. The attempts to obtain binderless films of La_2O_3 gave excellent results initially, but, within an hour after application, these films cracked extensively, completely lost adhesion to the substrate, and could not be reproduced. Lanthana is almost deliquescent, so that binderless films of it are not stable in any atmosphere containing moisture. The bulk of the samples prepared, consequently, were of alumina. Zirconia particle statistics ranged over several orders of magnitude and hence ZrO_2 was not considered seriously beyond the initial preparation state.

For most other materials hot spraying generally gave the best results. This technique involves preparing a liquid dispersion of the material and spraying it onto a heated substrate. There are many parameters in this technique, including the dispersant itself (e.g., water, ethyl, alcohol, isopropanol, hexane, methyl-ethyl ketone, etc.), the dispersing method (ball milling, stirring, ultrasonic energy, etc.), the gun-to-work geometry, the temperature of the substrate, and many others.

Normally, the procedure at first would involve simple (e.g. hand) mixing/stirring in an aqueous solution, and, if this was not successful, more elaborate procedures were attempted.

Most of the final materials described in the previous section have been wet-sprayed onto aluminum coupons, and the resulting binderless films have been characterized with respect to weight, thickness and spectral reflectance. Reproducibility became a problem almost immediately because the film density varied from one coupon to the next under apparently identical spraying conditions. As a result, we attempted to characterize films in terms of a "fluff factor," - the ratio of theoretical density of the crystalline solid to apparent film density. The apparent film density is calculated from the weight and thickness (average 8-10 readings) of the films deposited on a coupon which is 1.25 cm x 2.50 cm ($= 3.125 \text{ cm}^2$). For example, the apparent film density in the case of a film 0.0175 in (0.0444 cm) thick and weighing 0.100 gm is $0.1/(3.125 \times 0.0444) = 0.72 \text{ gm/cm}^3$. If this were an alumina film (density, 3.98 g/cm^3), the "fluff factor" would be $3.98/0.72 = 5.5$, which implies that the film is composed of 4.5 parts of voids to one part of material. Fluff factors as high as 6 to 8 have been obtained with Linde A. The importance of film density (or "fluff factor") has been evident, although the dependence of R_λ on it has not been quantitatively established. Also the effect of "fluff" has not been consistent. For example, a very "fluffy" coating generally loses reflectance when it is lightly compressed (e.g., by simple hand compaction); in other cases, lower reflectances have resulted from increasing "fluff factors." The difference may be that the fluff factor effect is itself a function of thickness or non-uniformity of "fluff." Not enough data have been collected to make reasonable judgements on either of these possibilities.

Close control of weight and thickness was gained by filtration and settling. Films deposited on millipore filters either by vacuum filtration in a Buchner Funnel or by simply allowing the material to settle out (over a period of several days) were

more uniform than films prepared by other methods. Another technique which gave fairly reproducible films made use of a calibrated eyedropper.

In one series of studies involving the scanning electron microscope (SEM) it was considered extremely important that, since the reflectance and SEM substrates were mutually incompatible, the samples for each be as nearly identical as possible. The eyedropper technique gave the best results in this case.

Eyedropper technique for preparing samples for SEM and reflectance measurements

5 wt% slurries of the various powders in distilled water were prepared in duplicate. One sample of each was dispersed by simple hand shaking of the bottles. The other sample of each was dispersed for 3 min. utilizing a Branson Sonifier.

Samples of each dispersion were transferred via an eyedropper to the surface of solvent cleaned stainless steel and aluminum substrates. In the case of the SEM substrate 1 cm diameter x 1 cm high cylinders were used. In the case of substrates for reflectance measurements, 1/2-in. x 1-in. x 1/4-in. thick aluminum coupons were used.

The bottles containing the slurries were shaken and while the powders were in suspension, samples were withdrawn by means of an eyedropper. The samples were immediately deposited on the metallic surfaces and allowed to air dry.

The amount of material deposited on the surface was such that the surface tension of the fluid just prevented it from flowing over the sides of the substrate, as in Figure 10.



Figure 10. EYEDROPPER APPLIED BINDERLESS FILMS

The pigment-vehicle films were prepared using E.I. DuPont de Nemours, Inc., methyl methacrylate polymer Elvacite 6011 and

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also General Electric Co.'s silicone polymer RTV 602. All of the paints made with these vehicles were ball-milled for a minimum of six hours.

F. SEM Test Procedure

The procedure we used in the SEM studies to examine the surfaces of samples was developed after it became clear what to look for in the photomicrographs. A standard procedure was adopted which simply involved looking at successively higher magnifications: 100X, 300X, 1000X, 3000X, 10,000X and 30,000X; in the rare cases of extremely fine particles (i.e., less than 0.1 μ) we used magnifications as high as 75,000X.

The rationale in this procedure developed from considerations of what information was desired from the studies. The purpose of the scans at 100X and 300X was to assure coating uniformity and representativeness. Depending upon the actual detail, a photomicrograph would be taken of some representative site at either 100X or at 300X, usually the latter. The size and shape of agglomerates and the general structure of the films was best established at either 1000X or 3000X depending upon actual agglomerate sizes. The sizes and shapes of discrete particles were best distinguished by studies at 10,000X and/or 30,000X.

Although there is a strong tendency to use higher and higher magnifications, we found that the lower magnifications gave the best results. If, from both a 10,000X and a 30,000X photomicrograph the particle size and shape could be resolved, we would choose the 10,000X photomicrograph, because it would give far better statistics; in this case we would be able to look at nine times $\left[= (30,000/10,000)^2 \right]$ as many particles.

In earlier studies, we keyed photomicrographs taken at high magnifications to those at lower magnifications. For example, if a particular agglomerate or a particular feature of it looked interesting we could "zoom in" on it at a much higher magnification and take a photomicrograph, and would then reference it with

respect to its location in the photomicrograph at the lower magnification. We abandoned this procedure because it became apparent that the location of a particular feature on one photomicrograph need not be identified on photomicrographs at different magnifications. In fact, the more representative a particular feature might be, the lesser the need to locate it on one photomicrograph with respect to another.

To summarize, we think SEM studies should be conducted at several levels of magnifications. The lowest levels should provide an idea of film uniformity and homogeneity. Intermediate levels should be used to discern agglomerate sizes, shapes, and general film structure, and the highest levels to study discrete particle sizes and shapes and the degree of agglomeration. Each level should be just adequate for reasonable discrimination and/or resolution in order that good statistics may also be obtained.

VI. EXPERIMENTAL RESULTS

A. Basic Objectives

The primary aim of the experimental program was, as mentioned previously, to correlate spectral reflectance with particle size. No such correlation, however, seems possible in dense powder films. Particle size has a dubious meaning, because particles rarely exist discretely, that is, unattached to or unassociated with any other particle or group of particles. Particle shape influences the surface electro-optical characteristics and thus the tendency to aggregate into much larger masses which very often have their own characteristic sizes and shapes. The basic light scattering behavior of a system of particles therefore depends on the action of individual, ("discrete") particles, the action of aggregated assemblies of them, upon their respective physical size and shape distributions, also upon their physical arrangement and how this is affected by the distributions of particle geometries. The expectation, therefore, that reflectance should be correlatable with particle size alone is not very realistic, because agglomerates are not particles, because particle size and shape strongly influence the geometry and statistics of the void spaces between particles and agglomerates, and because particle-particle, particle-agglomerate, and agglomerate-agglomerate separations are equally important parameters.

Particle size is obviously a prime parameter in single particle scattering phenomena; in multiple scattering, it is a compound parameter in the sense that it affects light scattering and reflectance in more than one way - both directly and indirectly.

B. Introduction

An important characterization shown with many of the reflectance spectra of binderless films, is the ratio of film weight (in grams) to film thickness (in inches). The inverse of this

ratio is a parameter directly related to the "Fluff Factor." In a unit area, the greater the deposited thickness for a given weight of a material, the "fluffier" it is. With very few exceptions, the fluffier (less dense) films have the higher reflectances. The first group of test results show, for example, spectra of binderless films with various fluff factors.

The term "undispersed" means that the powder material was used without any preparative treatment, except hand mixing. The term "dispersed" means that the powder material was dispersed in the liquid spraying vehicle by a sonifier treatment. Unless otherwise indicated, there is no difference in preparation or pretreatment between undispersed and dispersed materials except the sonifier treatment, and in both cases, the same vehicle is employed: distilled water, except as noted.

The second group consists of reflectance spectra of undispersed and dispersed films of various powder films and of their corresponding SEM photomicrographs.

In the third group of reflectance spectra scanning electron microscope (SEM) photomicrographs document the concept that voids are an important parameter in spectral reflectance.

The fourth group shows a series of reflectance spectra of films of Meller Alumina powders of various "particle sizes" in a pure methyl methacrylate binder (DuPont's Elvacite 6011) and also in a methyl silicone binder (G.E. RTV 602). Reflectance spectra are shown with particle size, PVC and film thickness as parameters. Transmittance spectra also appear in appropriate cases to show that an apparent loss of spectral reflectance does not necessarily imply an increase in spectral absorptance.

The fifth and final group consists of spectra of highly characterized films before and after 339 ESH of ultraviolet radiation (in vacuo) and after exposure to 625 Torr of O₂. The latter test series, conducted in IRIF-II, was intended to indicate the effect, if any, of particle size on the nature and extent of ultraviolet induced damage.

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The purpose of the above introduction has been to orient the reader in terms of what to look for in the experimental data. The results reported here, we believe, are representative; roughly one-fourth of all the reflectance spectra are shown, and perhaps the same fraction of the SEM pictures. To better fix one's ideas on the evaluation and/or study of these data, consider the following functional relationship for reflectance

$$R = R \left[m(=n_p/n_v), k, d_p, d_v, d_A, PVC, t, \lambda, \Phi_p, \Phi_v, \Phi_A \right]$$

The reflectance at any given wavelength depends respectively on m , the ratio of the indices of refraction of the pigment, n_p , and of the vehicle (binder), n_v ; k , the environment induced absorption-index; d_p , the average discrete particle size; d_v , the average void size; d_A , the average agglomerate size; PVC , pigment-vehicle concentration; t , film thickness; λ , wavelength; and Φ_p, Φ_v, Φ_A , in order, the average shapes of the particles, voids and agglomerates. With all of these data available for the binderless films, correlations of spectral reflectance with one or more of these individual parameters may be possible.

Except for n (or m) and k none of the parameters in the above expressions are basic. The grosser dimensions (particle size, for example) almost surely must be related to fundamental materials properties such as the distributions of electronic states. Classical electromagnetic theory, unfortunately, does not provide an adequate connection.

Finally then, in looking at the experimental data, we attempted to deduce the relationship between reflectance and the parameters stated in the above expression, as well as the relationships between the parameters themselves. For example, we have observed that particle size and shape and their distributions affect film packing density which in turn affects void sizes and their distributions, all of which affect spectral reflectance. Still another observation is that agglomerate sizes may depend on discrete particle size(s). The overall effect of either of these

may, in addition, be modified by n and k . It should become apparent then that light scattering in dense media does depend in part on particle size but not in any manner predicted by theory.

The use of diffuse spectral reflectance measurements to characterize binderless films in conjunction with other characterization methods provides a powerful tool for studying binderless films of materials. The SEM photomicrographs in particular complement the reflectance spectra in a very informative way. Before discussing them, let us first relate a few of the more detailed questions which these data were intended to answer. First, the reason for the very wide spectral region in which many materials exhibit high reflectance is puzzling; it could not be attributed simply to particle size or to size distribution. Theory would predict a much smaller effective region. Secondly, the effect of scattering on intrinsic absorption had to be studied; would scattering increase or decrease the reflectance optical density when absorbers are present?

All of the binderless films discussed, unless it is stated otherwise, have been sprayed onto aluminum coupons from aqueous suspension. The samples whose reflectance and thickness (or film density) properties have been compared were prepared on the same day as they were measured. The reader may find helpful Table 4 which identifies the materials we are discussing and summarizes particle size data. Finally, the discussions and remarks here are based on analyses of the original spectral data in which the spectral regions $0.25-0.35\mu$, $0.325-0.7\mu$ and $0.7-2.60\mu$ were each recorded on separate charts - the standard Beckman DK-2A chart records.

C. Discussion of Test Results

1. Group I

Figure 11 shows the reflectance spectra of samples of ZnS which have been wet-sprayed onto aluminum coupons. The sample

Table 4

PIGMENT MATERIALS DESIGNATIONS AND PARTICLE SIZE DATA

Material	Designation	$\bar{d}_p$		d_p Range ³	BET		Porosity
		Mfg. 1	IITRI 2		m ² /g	$\bar{d}_p$ ⁴	
Linde A	LA	0.3	0.3	0.1 -0.8	9.18	0.16	93.6
Linde C	LC	1.0	0.62	0.25-1.0	3.07	0.49	93.6
Meller 0.06	M-0.06	0.06	0.06	0.01-0.1			
Meller 0.3	M-0.3	0.3	0.2	0.05-0.3			
Meller 1.0	M-1.0	1.0	0.4	0.2 -0.6			
Meller 3.0	M-3.0	3.0	0.5	0.2 -0.8			
ZrO ₂							
TAM-548	Zr-548	4.0	0.35	0.15-0.7			
ZnS	ZnS		0.15	0.05-0.4			
La ₂ O ₃ 529.9	La-9.9		0.25	0.05-0.5			
Cab-O-Sil	L-5		0.05				
Pore Sizes							
Millipore SS	MP-3	0.3 ±0.02		4-6			
Millipore PH	MP-0.3	0.3 ±0.02		0.5 -1.0			
Millipore RA	MP-1.0	1.2 ±0.3		2.5 -3			

¹The average or nominal particle size claimed by manufacturer.

²The average or nominal particle size determined at IITRI from SEM and TEM pix.

³Same as "2" above except that range is smallest to largest particle.

⁴Effective diameter based on BET surface area.

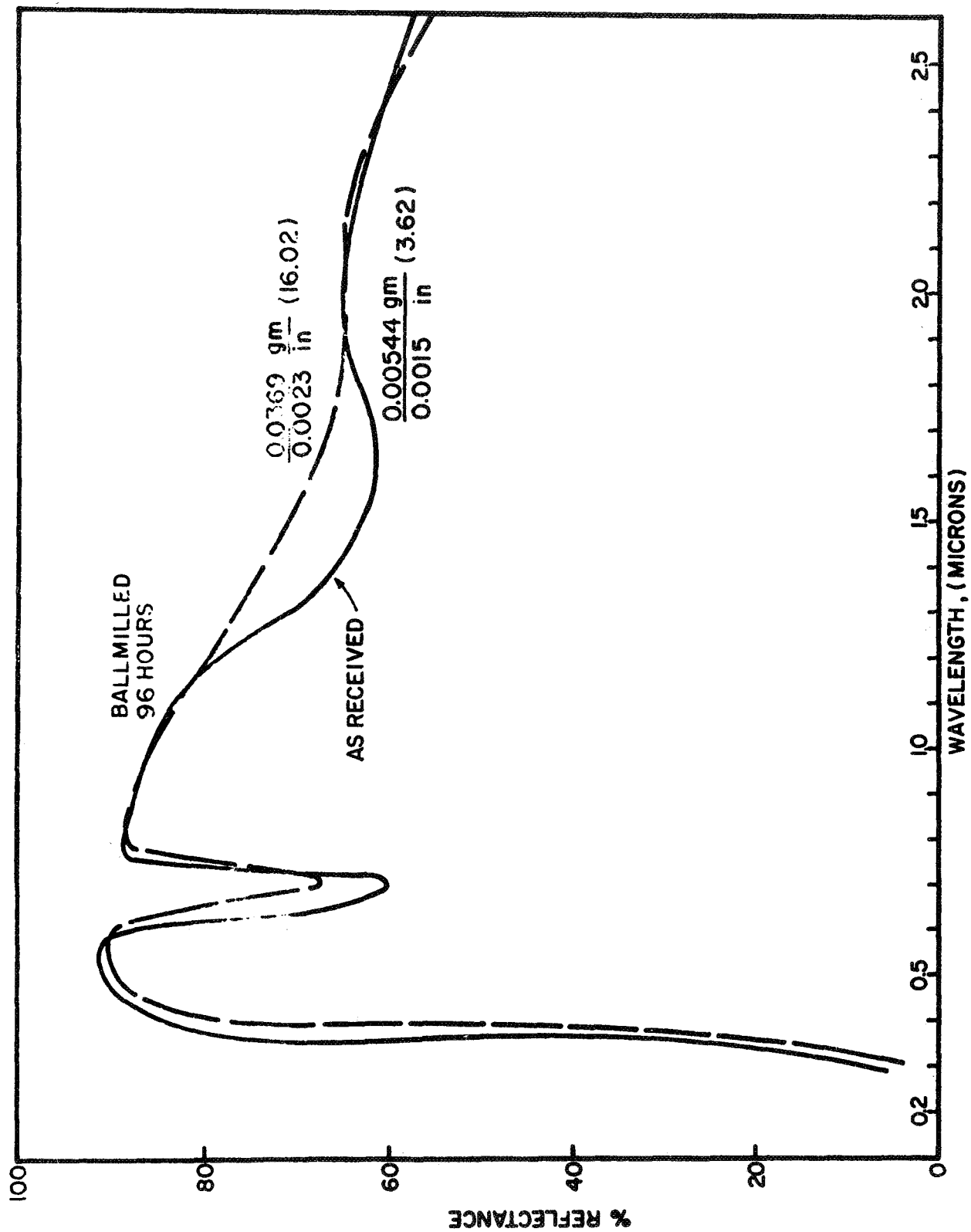


Figure 11. REFLECTANCE SPECTRA OF BINDERLESS ZINC SULFIDE
(EFFECT OF 96 HR BALL MILLING)

prepared by hand dispersion (no ball-milling) obviously has a greater absorption effect at 0.72μ than the sample which was ball-milled for 96 hrs. The reflectance values near the 0.72μ absorption band are very close, but the dip in the spectrum of the sample prepared from untreated ZnS at 1.5μ may suggest a shift of the scattering from this wavelength region to that near the 0.72μ absorption system. The SEM photomicrographs (hereafter called pix) show that ball milling did not affect the particle size, it broke up some of the larger aggregates, and the resulting coating was more smooth. Figures 12 and 13 are SEM pix at 10,000X of ZnS films, untreated and dispersed, respectively. The compactness of the ball-milled coating is indicated by its high film density factor (16 vs 3.6 for the untreated sample). Unfortunately, SEM pix at magnifications lower than 300X were not taken, so that the size distributions of the aggregates before and after dispersion could not be assessed. Approximately 10 other ZnS spectra were obtained and the results are typical of those shown in Figure 11.

The spectra of ZrO_2 samples display a trend which is unique among all the samples studied; the reflectance increases with increasing film density. In Figure 14, the fluffiest film (with a film density factor of 12.9) has the lowest overall reflectance. The only difference between these coatings is the weight and thickness. They were applied simultaneously; the first coupon was removed from the spray path after about 10 passes; the second one, after about 12 passes; and the third, after about 14 passes. Apparently thickness differences do not explain the reflectance differences; the top two spectra are of the same thickness.

Cab-O-Sil L-5, as we noted earlier cannot be applied in binderless form at thicknesses sufficient for opacity. As Figure 15 shows, the spectral reflectances of several films of this material peak at about 0.4μ . The manufacturer's TEM pix show that this material has a very uniform discrete particle size of 0.05μ , and that these particles are loosely associated in chains of about 1000-10,000 particles each. The index of refraction of

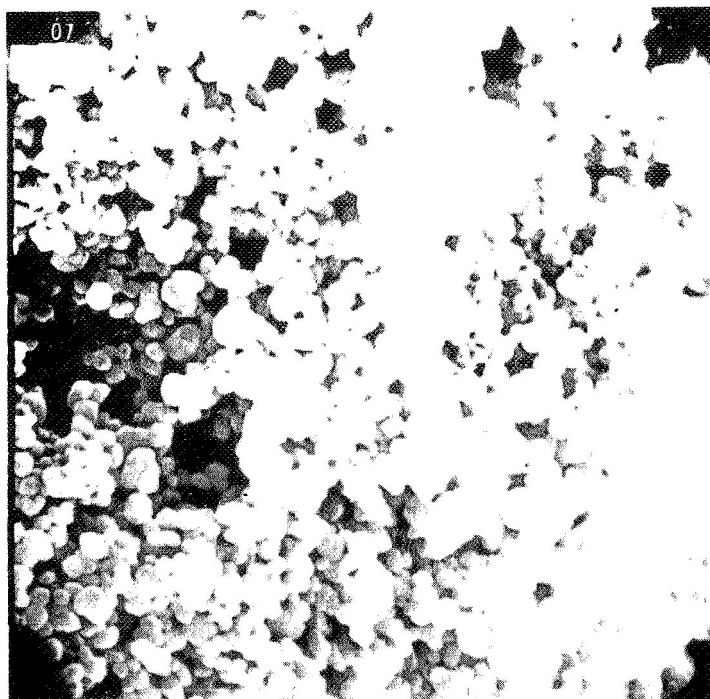


Figure 12. SEM OF ZnS-U (10,000X)

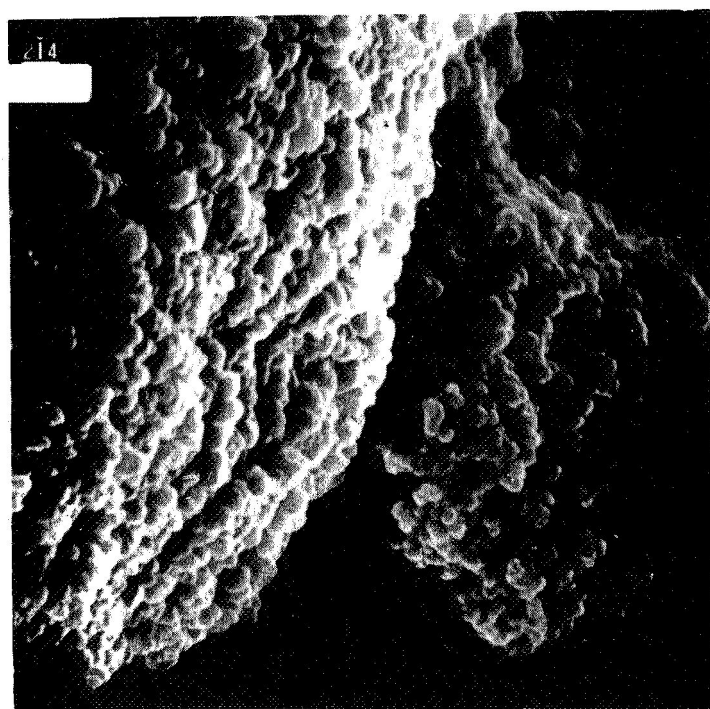


Figure 13. SEM OF ZnS-D (10,000X)

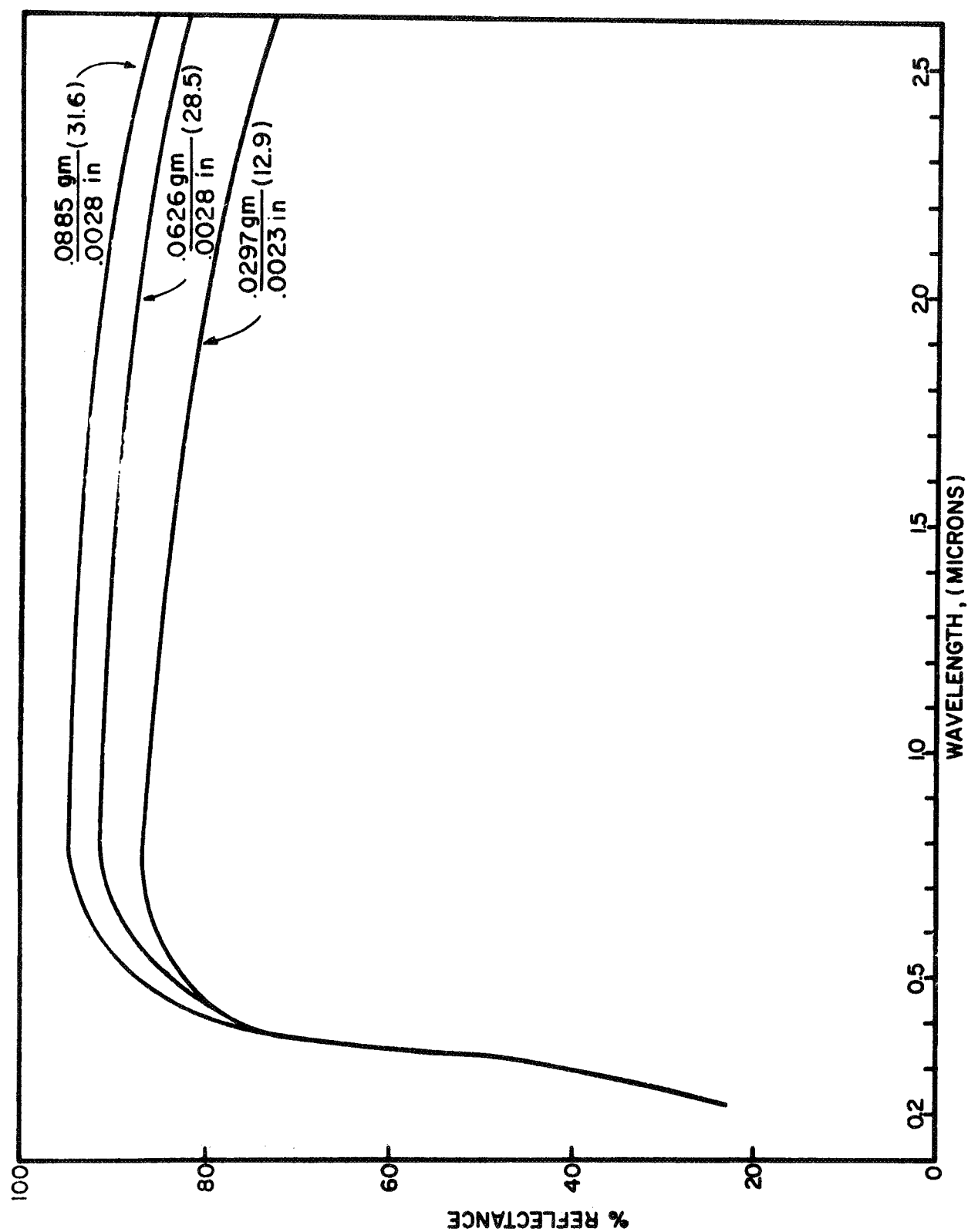


Figure 14. REFLECTANCE SPECTRA OF BINDERLESS ZrO_2
(TAMS HP4548)

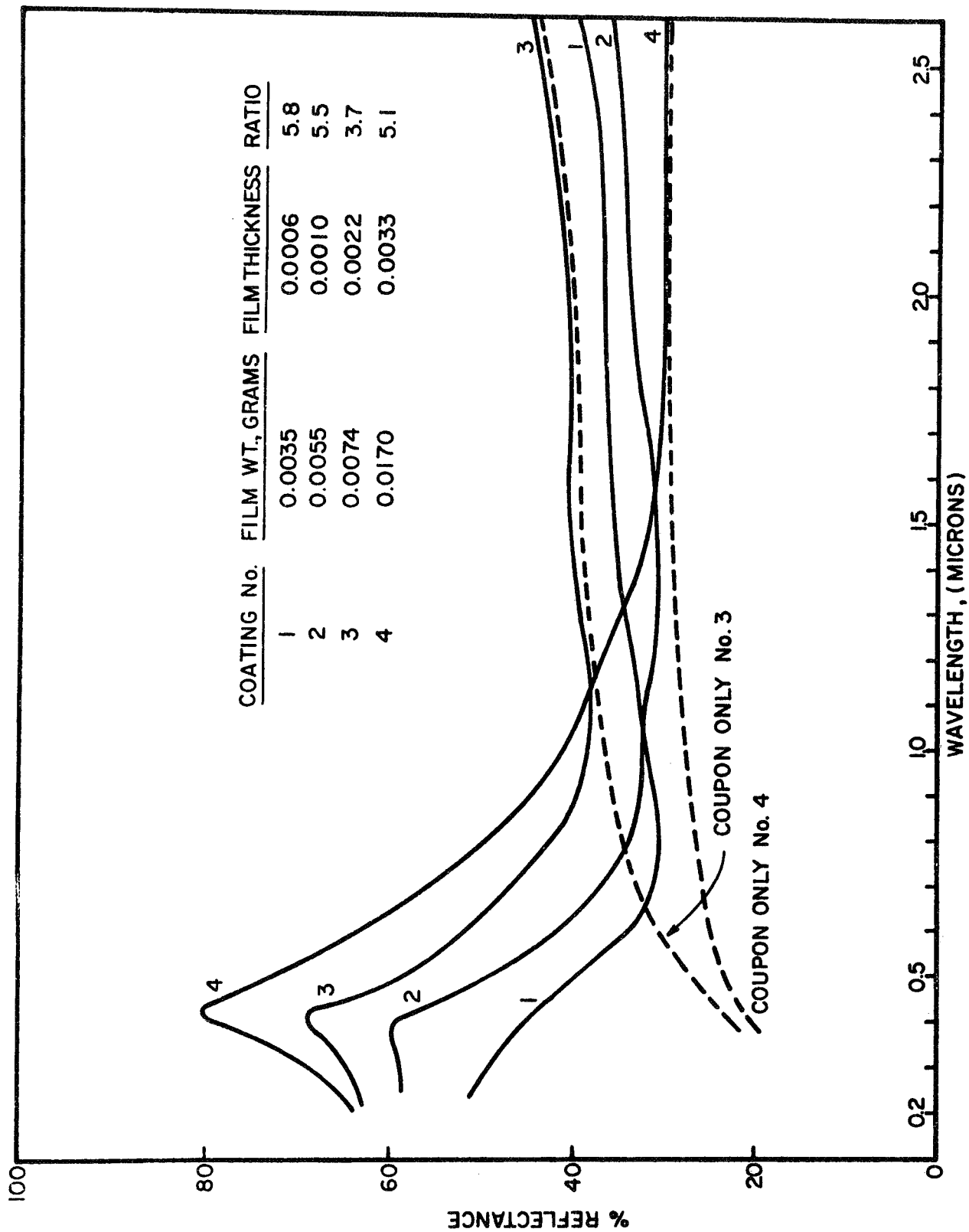


Figure 15. REFLECTANCE SPECTRA OF BINDERLESS CAB-O-SIL L-5 (SiO_2)

Cab-O-Sil (a very pure silica) is very low and hence high spectral reflectance values are not expected. Comparing the spectra of Figure 15 with those of the base coupons showed that the Cab-O-Sil spectra in the range between 1.0 or 1.25μ and 2.6μ is essentially that of the coupons; the spectra on the short wavelength side of 1.0μ are definitely due to Cab-O-Sil. The reflectance peaks show an inverse dependence on film density factor: the less the film density factor, the higher the reflectance - except for the top-most curve which is significantly thicker and heavier than the others.

Aqueous spray coatings of lanthana failed consistently. This material is hygroscopic and changes its physical surface properties drastically upon coming in contact with water. The films deposited from aqueous sprays initially appeared very good but within a few minutes after drying they became non-adherent. The films of lanthana whose spectra are shown in Figures 16 and 17 were obtained by spraying absolute ethanol and isopropanol suspensions, respectively. These films also failed eventually and great care had to be taken to prevent and/or minimize their exposure to water vapor. A most interesting feature of these spectra is the presence in the case of ethanol sprayed coatings, and absence in the other, of the absorption band at 1.4μ . The fact that in the ethanol case the Code 529 Lanthana has a generally higher reflectance, and in the isopropanol case, a lower one, is most likely due to thickness. The crossover of the spectra at 2.3μ is probably due to different combinations of adsorbed water or OH^- groups.

2. Group II

The reflectance spectra just discussed and many others along with them together with their SEM pix have suggested that voids can also reflect. In Figures 18 and 19 we have shown the reflectance spectra of five different millipore filters. Figure 19 is a partial repeat of Figure 18 using different specimens, to check reproducibility. As the SEM pix (Figures 20, 21, 22, 23, 24 and 25) attest, the major difference between these filters is the

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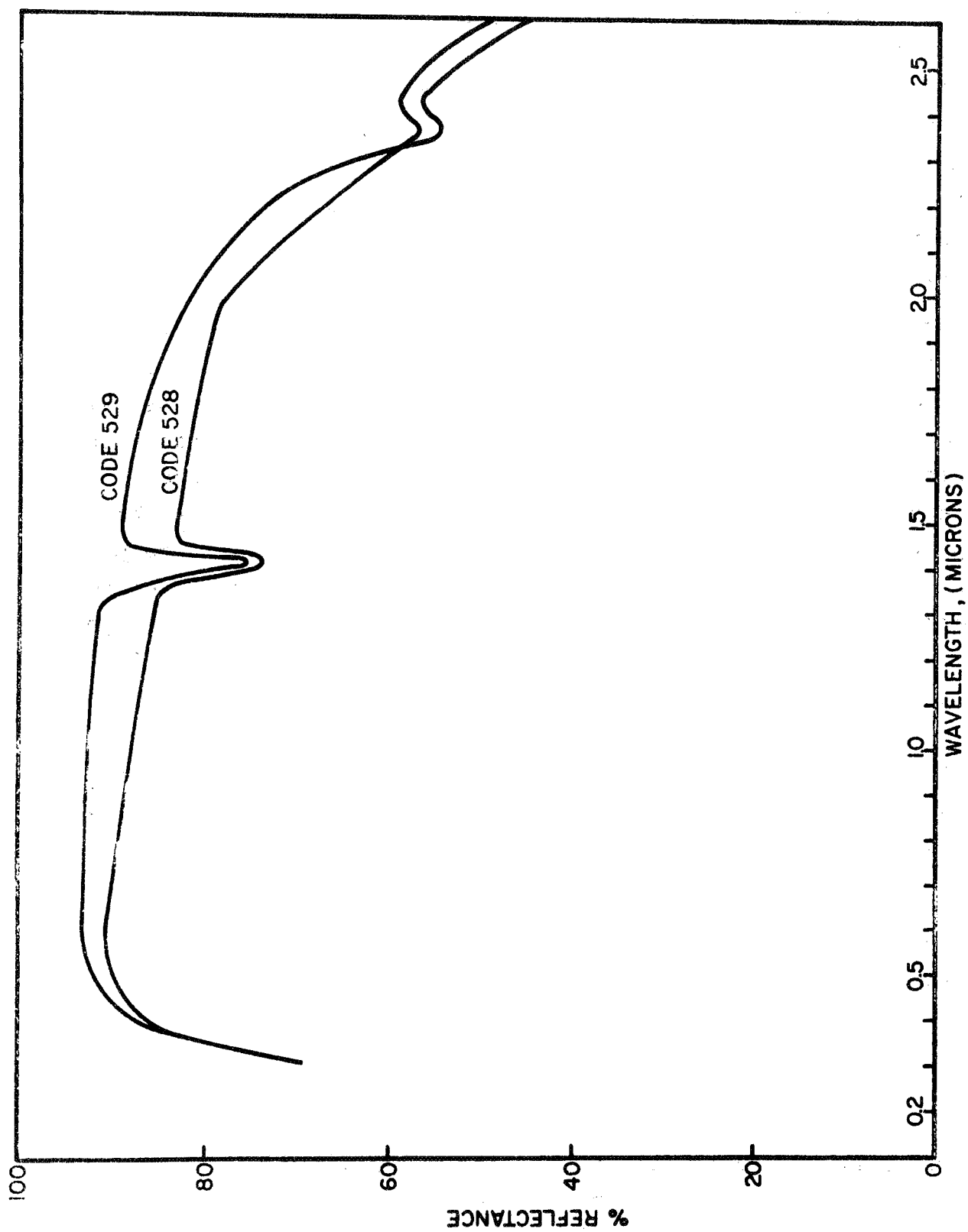


Figure 16. REFLECTANCE SPECTRA OF BINDERLESS La_2O_3 - CODES 528 AND 529
(Ethanol Vehicle)

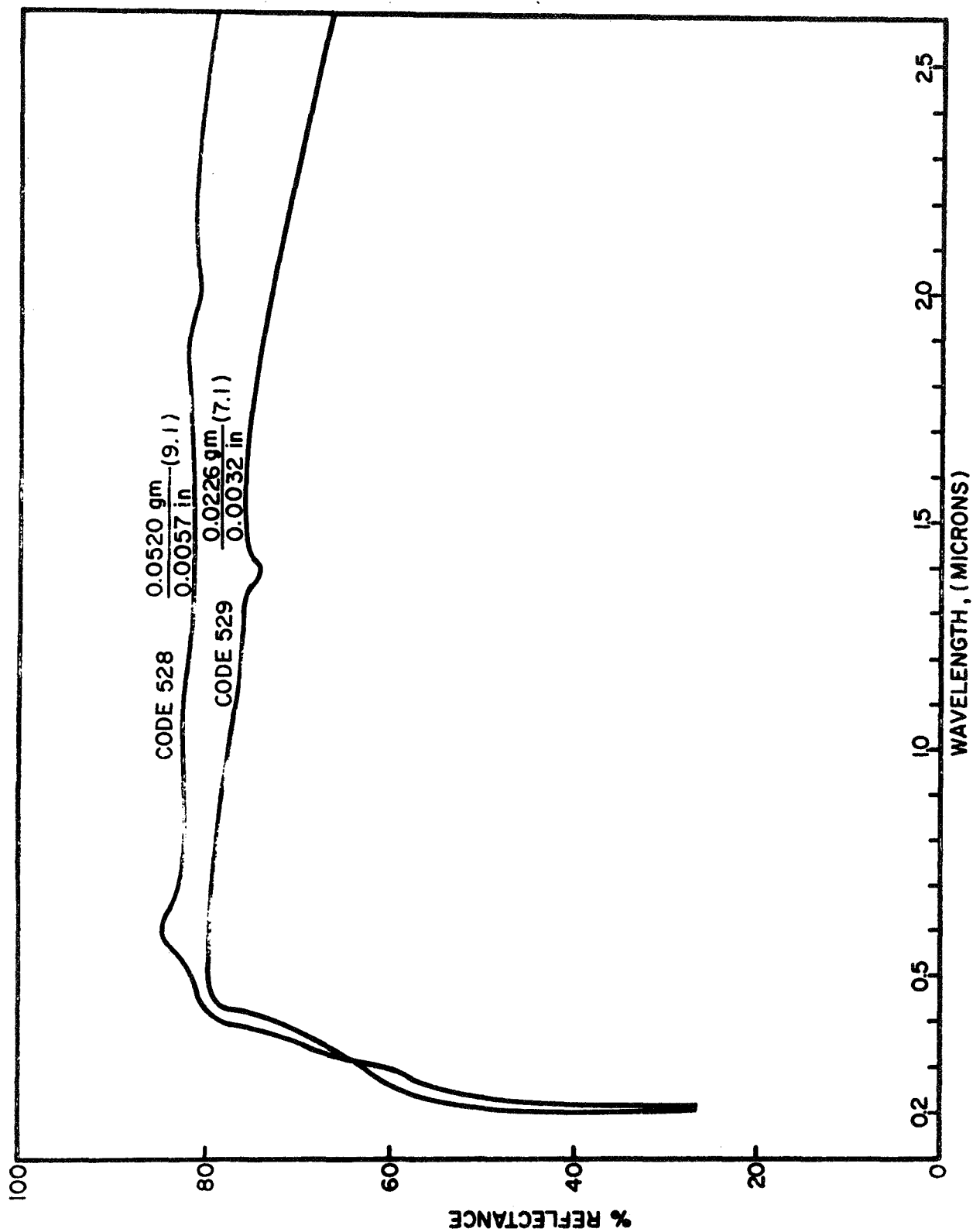


Figure 17. REFLECTANCE SPECTRA OF BINDERLESS La_2O_3 - CODES 528 AND 529
(Isopropanol Vehicle)

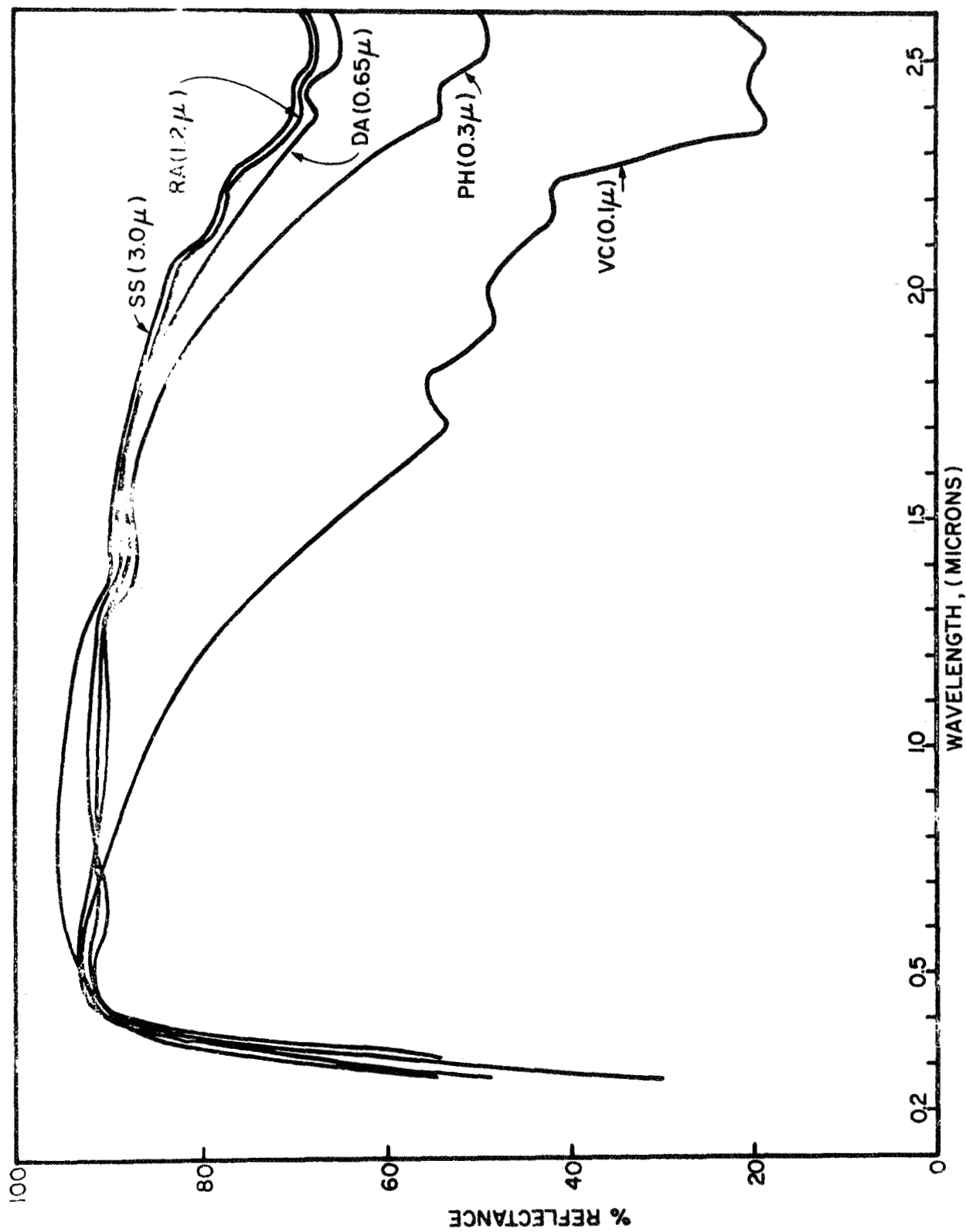


Figure 18. REFLECTANCE SPECTRA OF MILLIPORE FILTERS - TYPES VC, PH, DA, RA AND SS

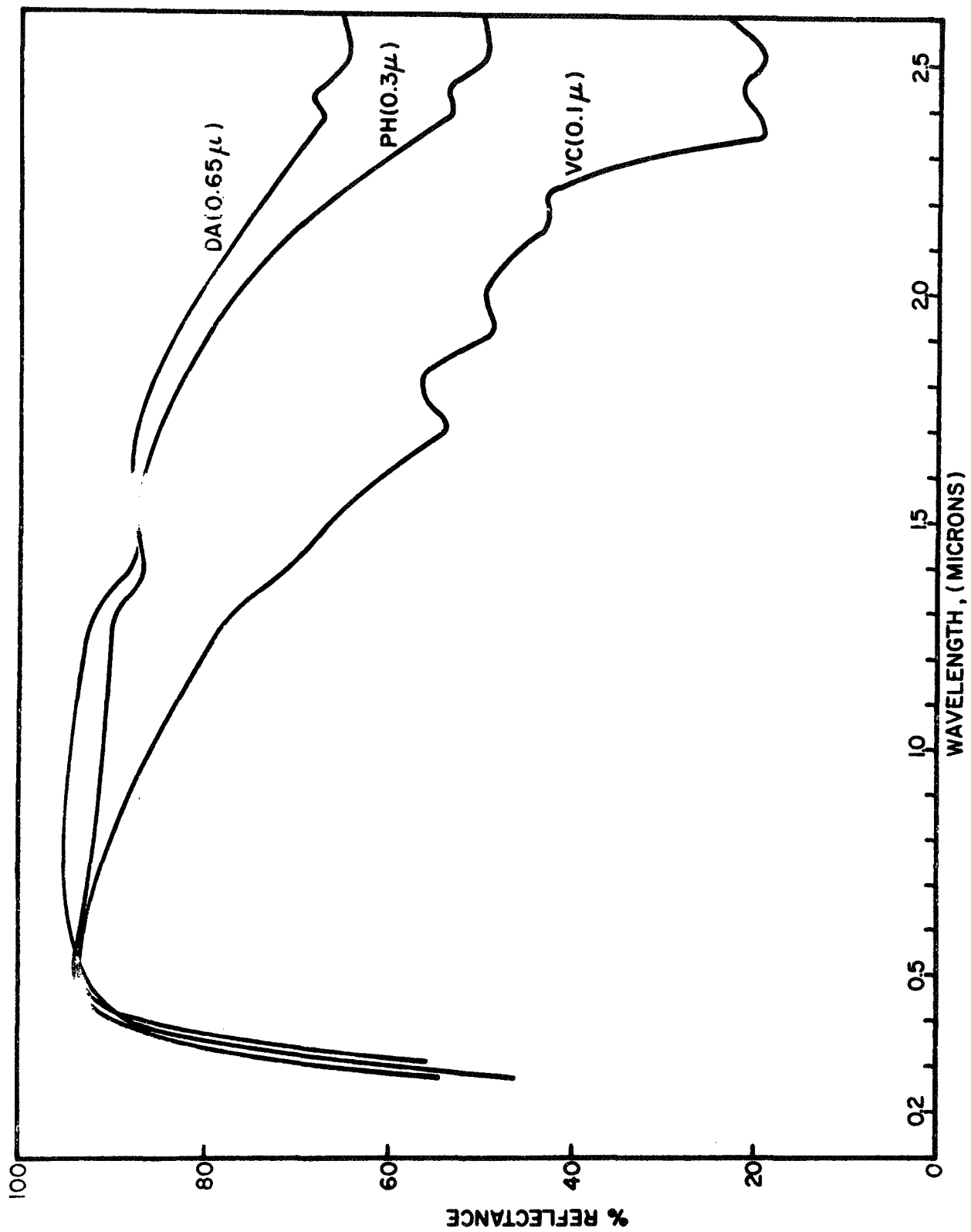


Figure 19. REFLECTANCE SPECTRA OF MILLIPORE FILTERS - TYPES VC, PH AND DA

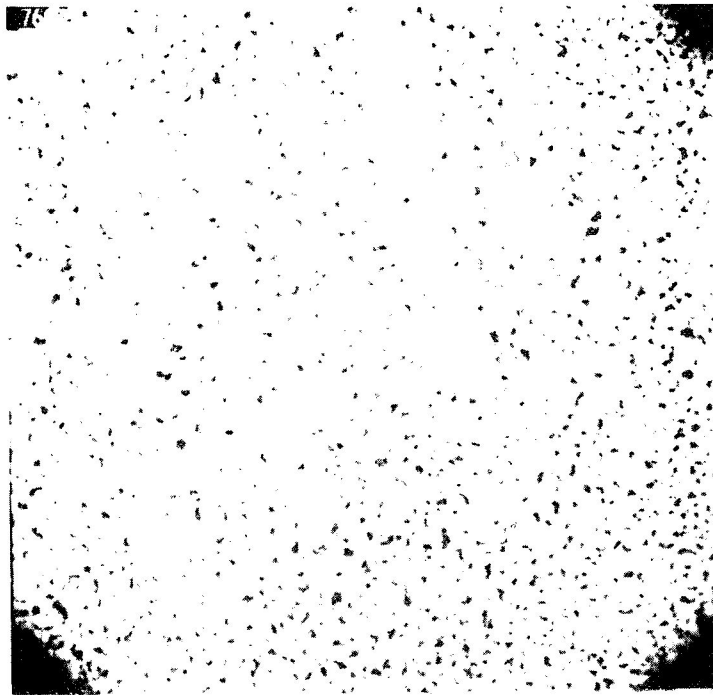


Figure 20. SEM OF 0.3 μ MILLIPORE FILTER TYPE PH (1,000X)

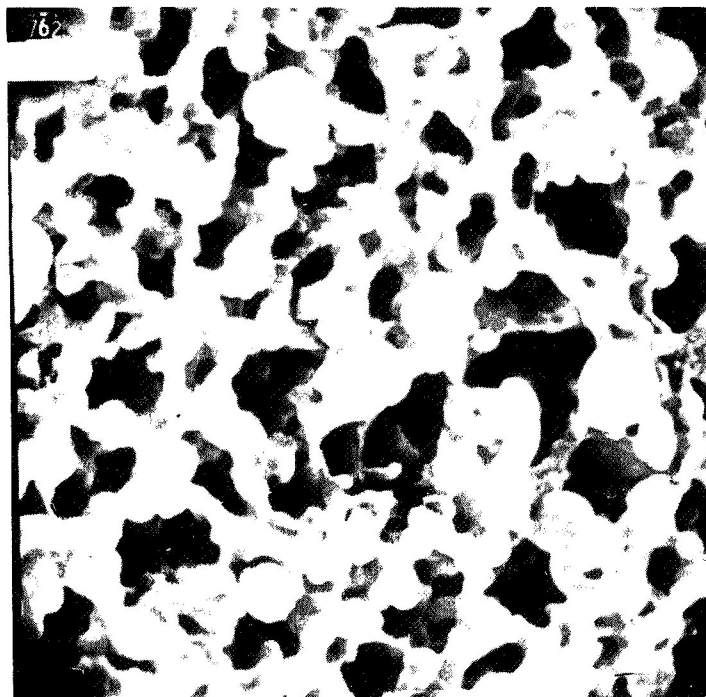


Figure 21. SEM OF 0.3 μ MILLIPORE FILTER TYPE PH (10,000X)

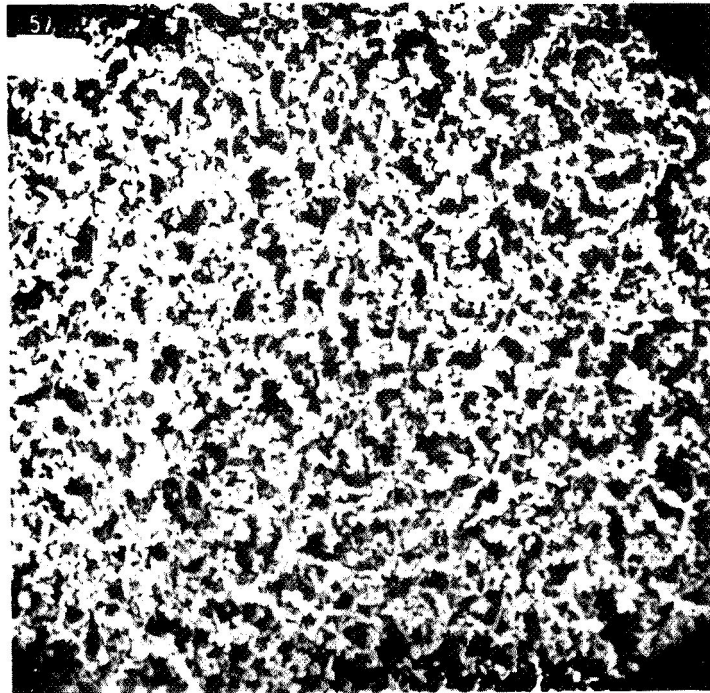


Figure 22. SEM OF 1.2 μ MILLIPORE FILTER TYPE RA (1,000X)

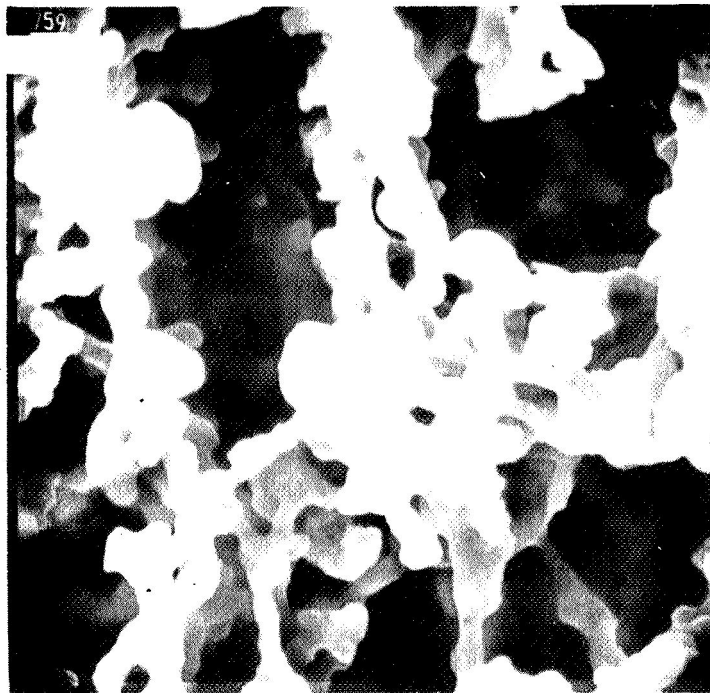


Figure 23. SEM OF 1.2 μ MILLIPORE FILTER TYPE RA (10,000X)

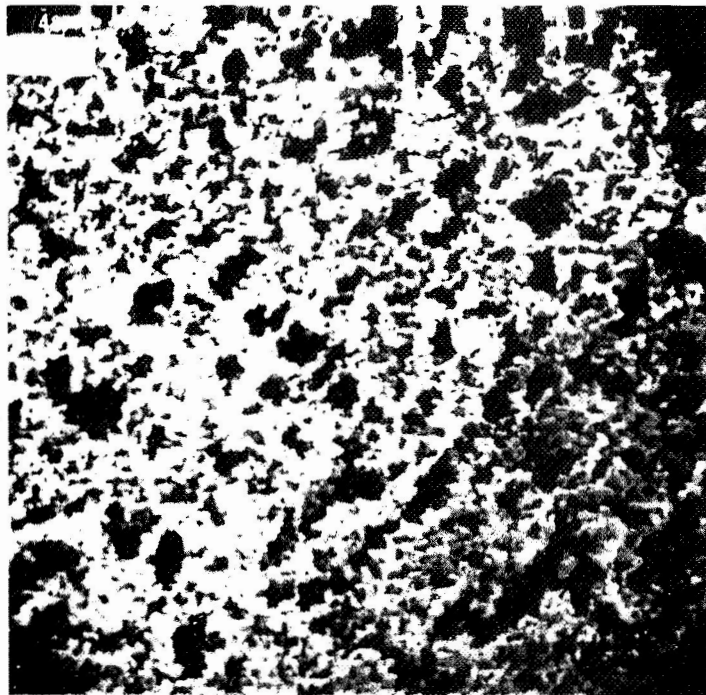


Figure 24. SEM OF 3.0 μ MILLIPORE FILTER TYPE SS (1,000X)

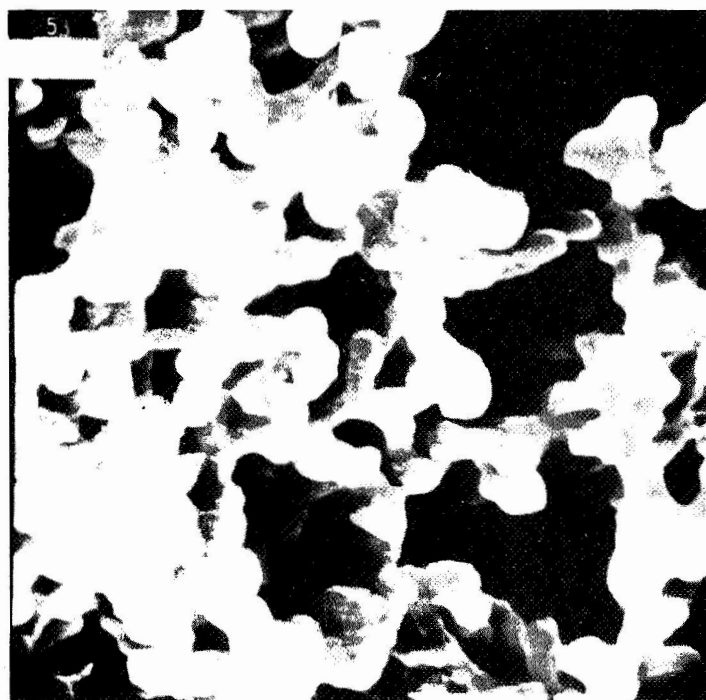


Figure 25. SEM OF 3.0 μ MILLIPORE FILTER TYPE SS (10,000X)

void space. The particle or fiber geometry is very uniform (eight SEM pix at various magnifications from 1000X to 20,000X taken of the type SS (nominally 3.0μ) Millipore filter, for example, showed extremely good uniformity). The reflectance spectra behave as expected from theory: at the longer wavelengths the smaller pore size materials reflect least - and so on. Even though it is not evident in these Figures, due to scale compression, the spectral reflectance in the visible and ultraviolet regions show that the smaller pore size materials are the most reflective in this region. The combination of reflectance spectra and SEM pix has in this instance, conclusively demonstrated the importance of light scattering due to voids. It might even be possible to obtain quantitative correlations from these data, that is, correlations of void size with spectral reflectance, since the SEM pix show consistent particle and void sizes from one filter size to another.

3. Group III

This group of binderless films is concerned with two different alumina products - one made by Linde, the other by the Adolf Meller Co. All are, according to their suppliers, $\alpha\text{-Al}_2\text{O}_3$. Figure 26 compares the reflectance spectra of Meller's 0.3μ alumina (M-0.3) with Linde A (LA). Note the considerably higher reflectance of M-0.3, its lower film density factor, and the comparable thicknesses. An undispersed and dispersed sample of LA are compared in Figure 27. Here, it seems that both thickness and fluff are important.

Figure 28 exhibits some very interesting spectra of undispersed Linde C (LC). Compare the spectrum with a film density factor of $0.0163/0.0026$ ($= 6.3$) with that whose film density factor is $0.0024/0.002$ ($= 12.0$). These spectra provide conclusive evidence of the effects on reflectance of voids. The spectral effect of reflectance/scattering is clearly present. Above all, however, it is obvious that both thickness and void structure are important. The major scattering effect (at least as manifest

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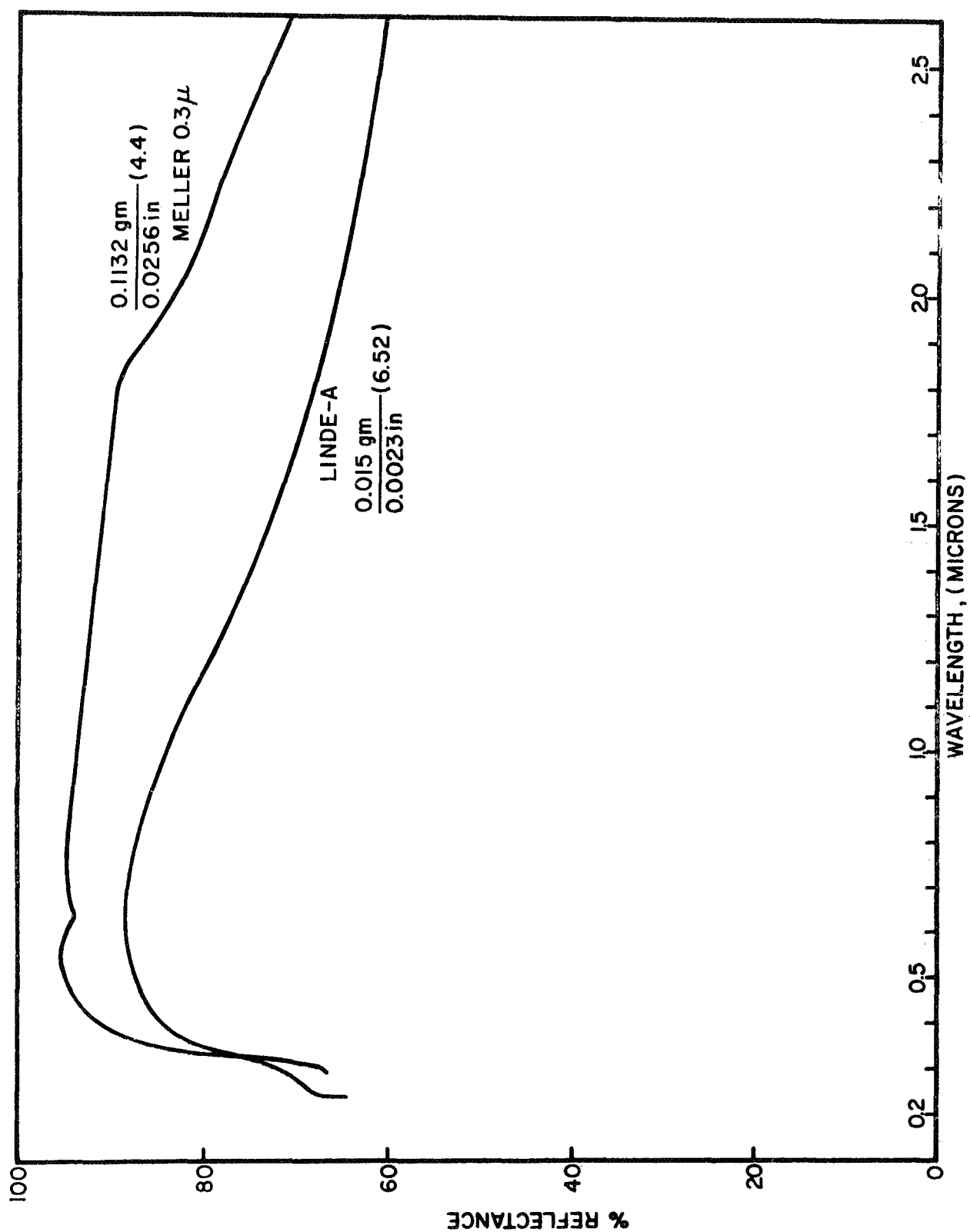


Figure 26. REFLECTANCE SPECTRA OF BINDERLESS Al_2O_3
MELLER 0.3 μ VS. LINDE A

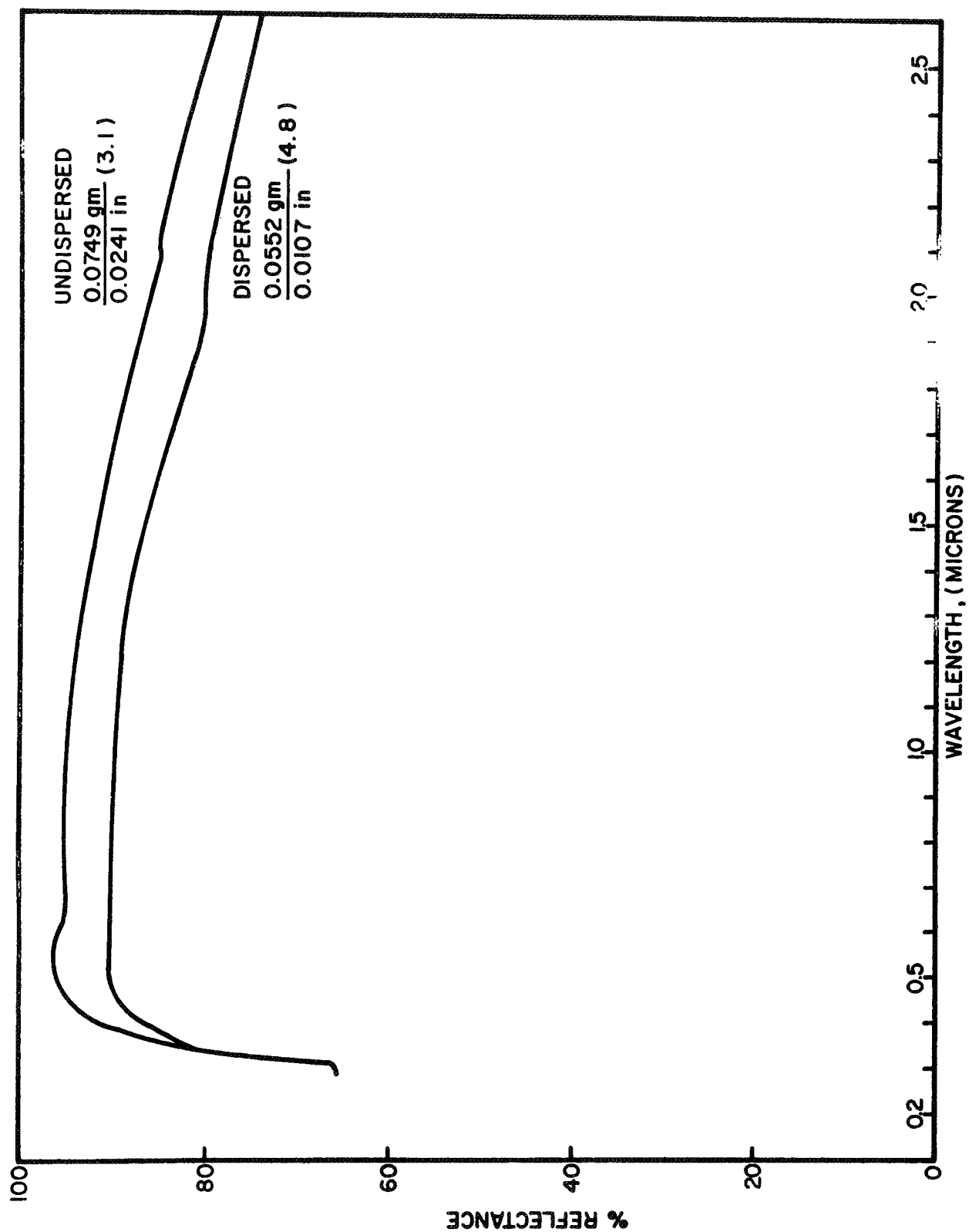


Figure 27. REFLECTANCE SPECTRA OF BINDERLESS LINDE A (0.3 μ) Al_2O_3 DISPERSED VS. UNDISPERSED

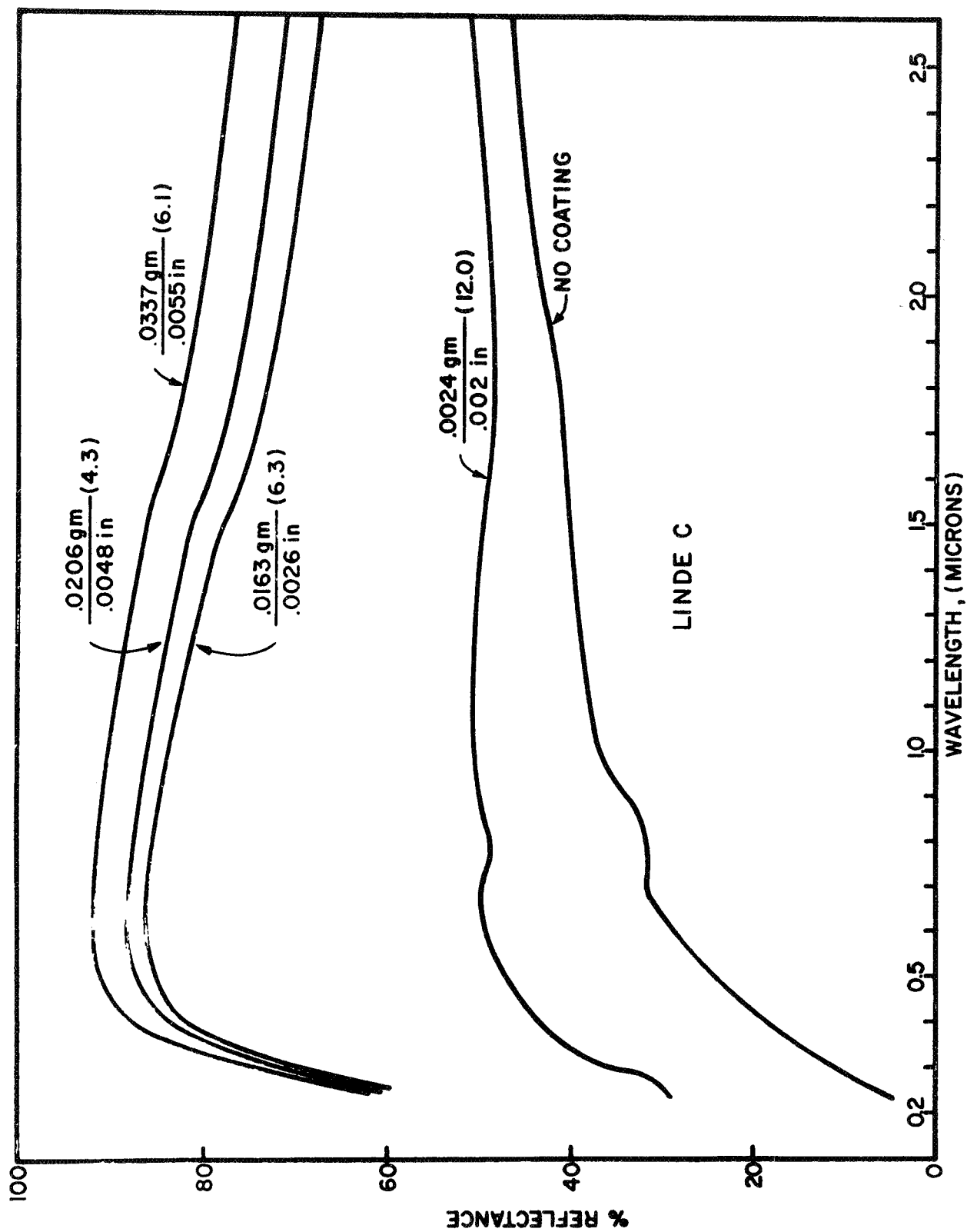


Figure 28. REFLECTANCE SPECTRA OF BINDERLESS LINDE C (1.0 μ) Al_2O_3 VS. THICKNESS

by differential reflectance spectra) occurs in the visible region near 0.6μ - which incidentally is the IITRI-determined average particle size of LC.

Spectra of LA (undispersed) and LC (undispersed) in Figure 29 show that the spectral reflectance peak for LA is at a shorter wavelength than that for LC, (note the crossover at 0.78μ), as one would expect from theory. The SEM pix of these two materials, Figures 30 and 31 vs Figures 32 and 33, indicate that LA has more voids and slightly smaller aggregates on the average. The aggregates of LA, as Figures 34 and 35 clearly show, consist of fine particles, whose sizes and shapes will be left to the reader to determine and characterize. Figure 36 may be of some help in that effort. Referring back to Figure 34, a portion of the very subtle edge which runs slightly upward from the lower lefthand part of the picture has been blown up from 3000X to 10,000X in Figure 35. At the top shelf of the ledge (just above the edge) and roughly 1/3 the way from left to right and a quarter of the way up the picture is a small hole, which appears also in the upper left corner of Figure 35. Figure 36 (30,000X) is a blowup of a section located on the edge in Figure 35 very near the vertical centerline of the picture. The aggregates resemble plates and are $4-6\mu$ thick and $45-60\mu$ long. In Figure 32, note that the void spaces in between aggregates are quite variable in size - roughly $5-30\mu$.

The spectra for three specimens of Meller's 1.0μ Alumina (M-1.0) in Figure 37, demonstrates again the importance of fluff. The very high reflectances obtained suggest that the differences between the spectra are not due to thickness but rather to the fluff factor. The SEM pix of this material, Figures 38, 39 and 40 look very much like those of LA, except that, as one can appreciate by comparing Figure 38 with Figure 32, M-1.0 has a preponderance of smaller aggregates and their fragments. Comparing their spectra we see that the M-1.0 material has better infrared reflectance. As with the LA pix, the reader will be left to provide his own descriptions of the particles in Figure 40.

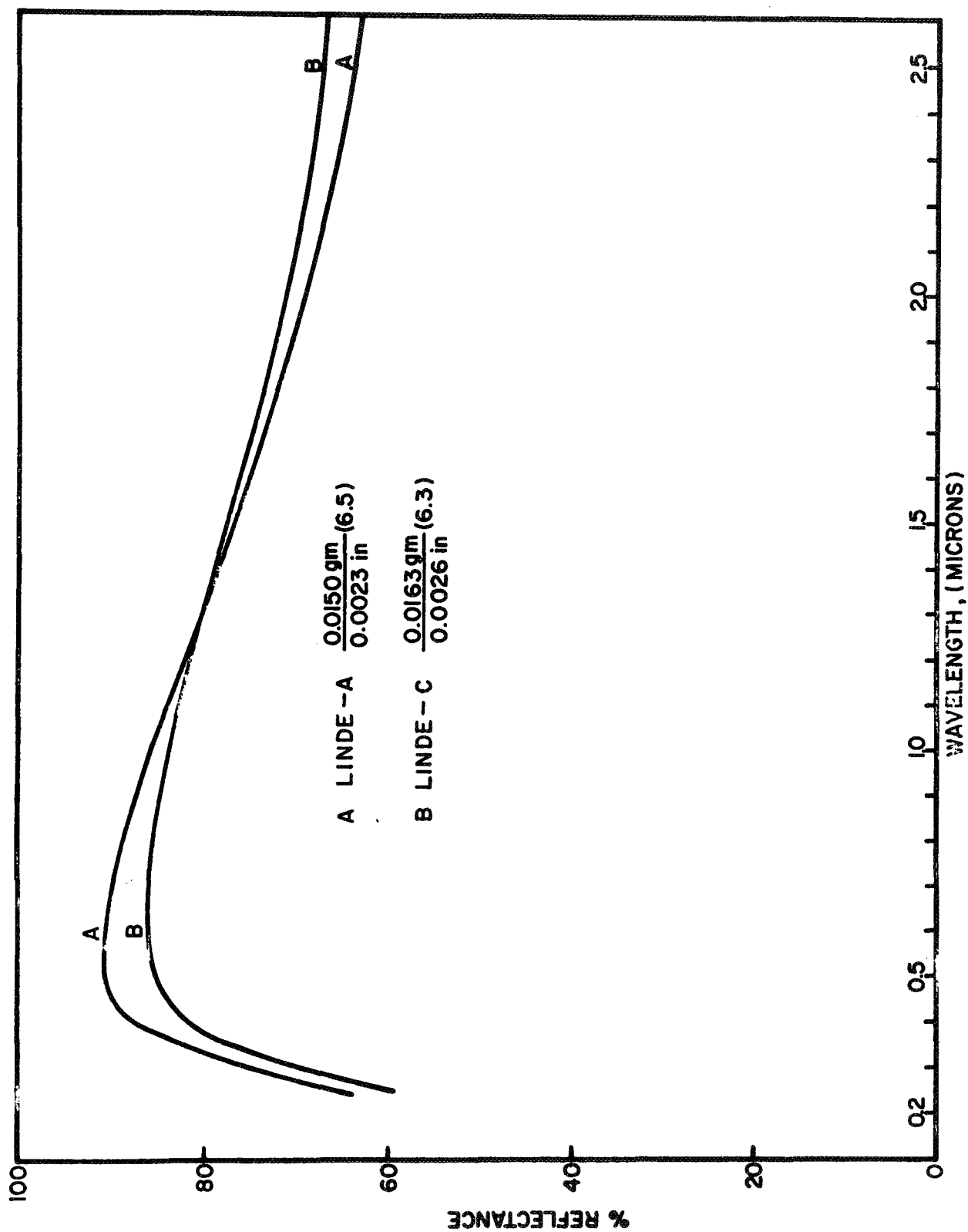


Figure 29. REFLECTANCE SPECTRA OF BINDERLESS Al_2O_3
 LINDE A (0.3μ) VS. LINDE C (1.0μ)

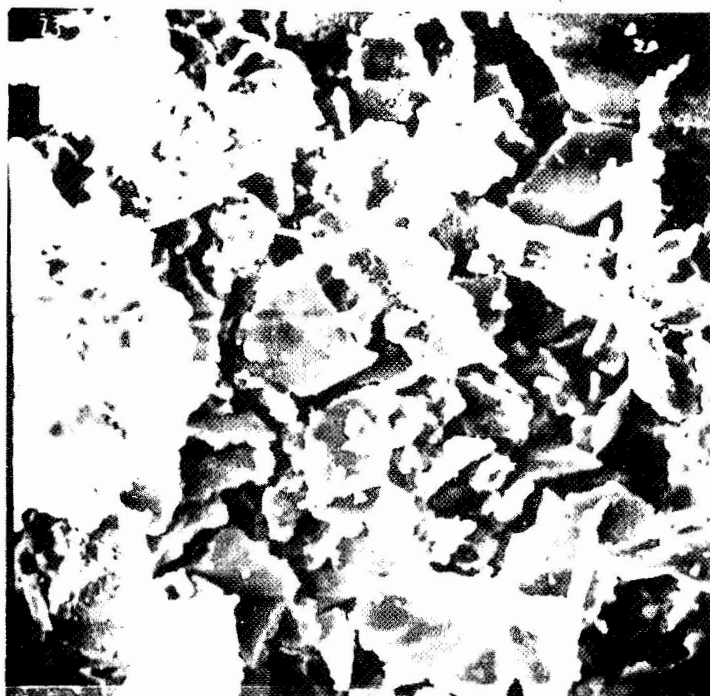


Figure 30. SEM OF LINDE C-U (300X)

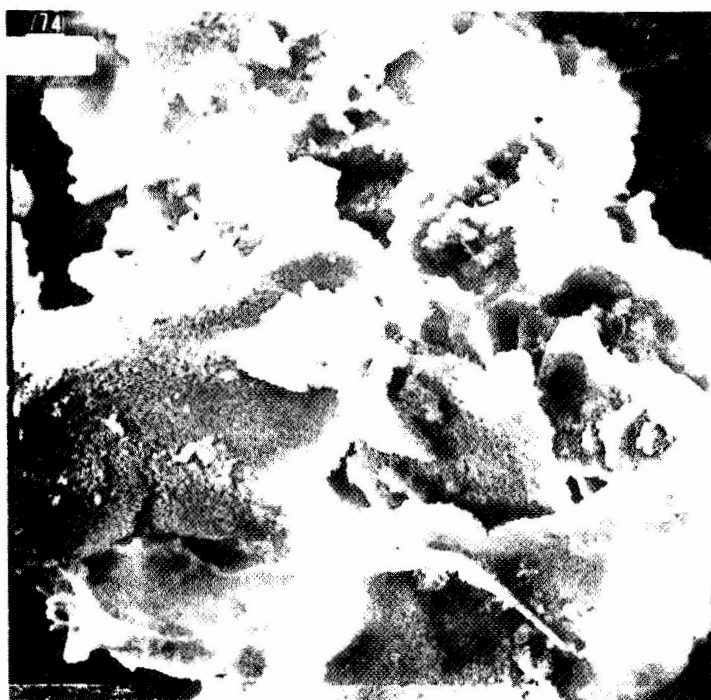


Figure 31. SEM OF LINDE C-U (1,000X)



Figure 32. SEM OF LINDE A-U (300X)

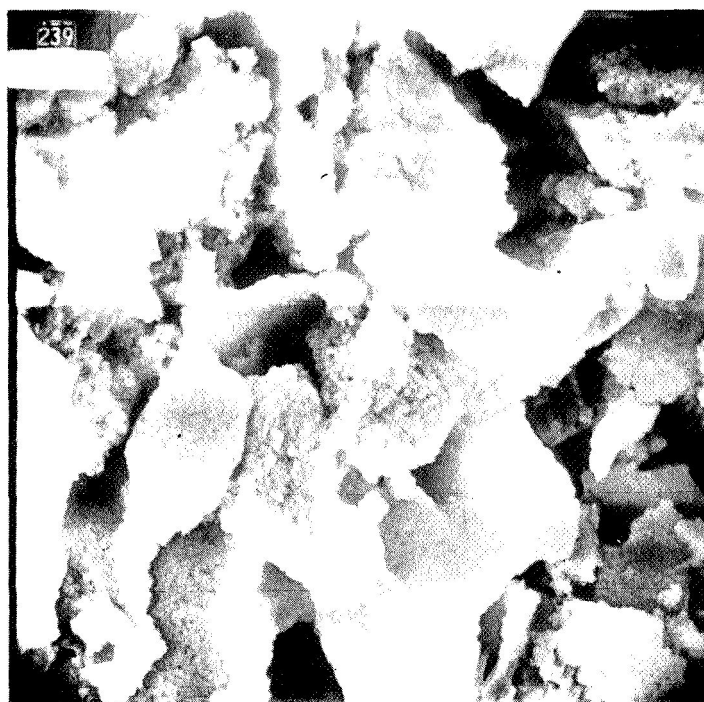


Figure 33. SEM OF LINDE A-U (1,000X)

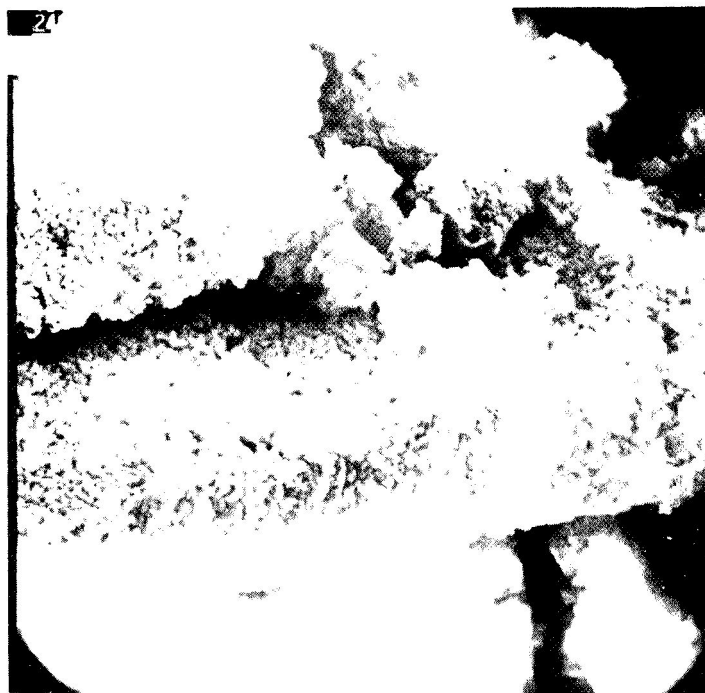


Figure 34. SEM OF LINDE A-U (3,000X)

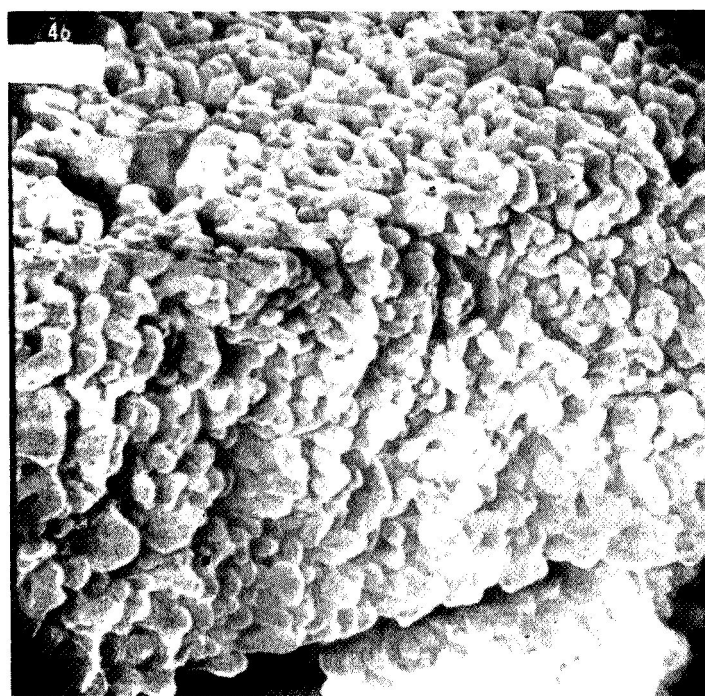


Figure 35. SEM OF LINDE A-U (10,000X)

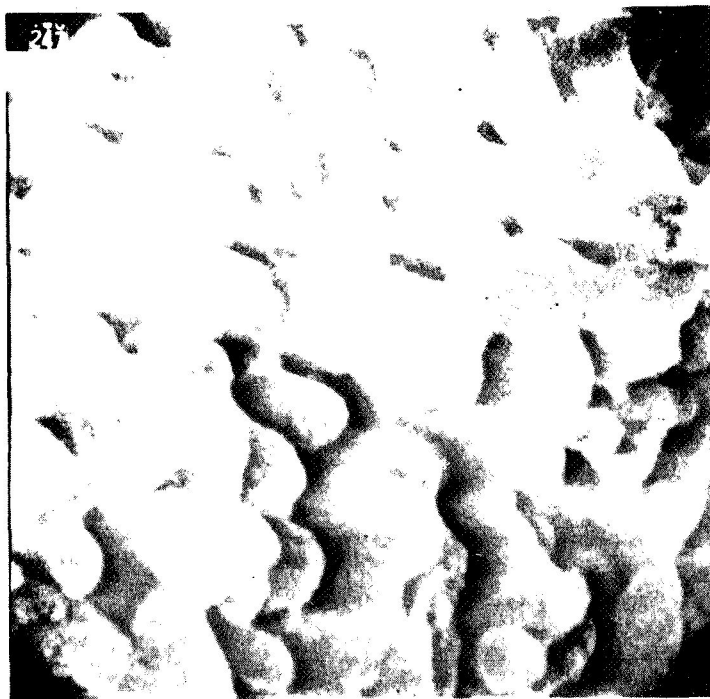


Figure 36. SEM OF LINDE A-U (30,000)

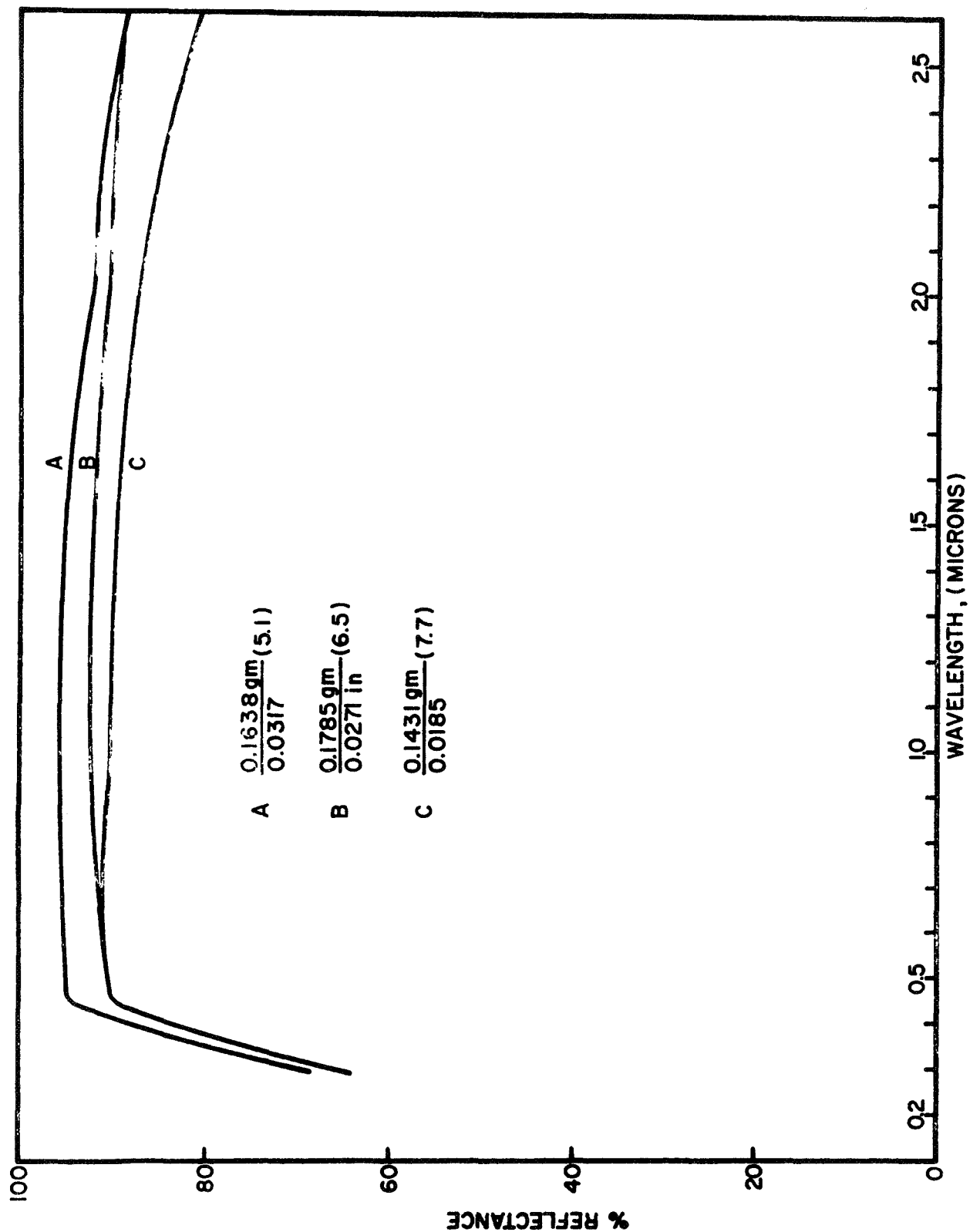


Figure 37. REFLECTANCE SPECTRA OF BINDERLESS MULLER 1.0μ Al₂O₃

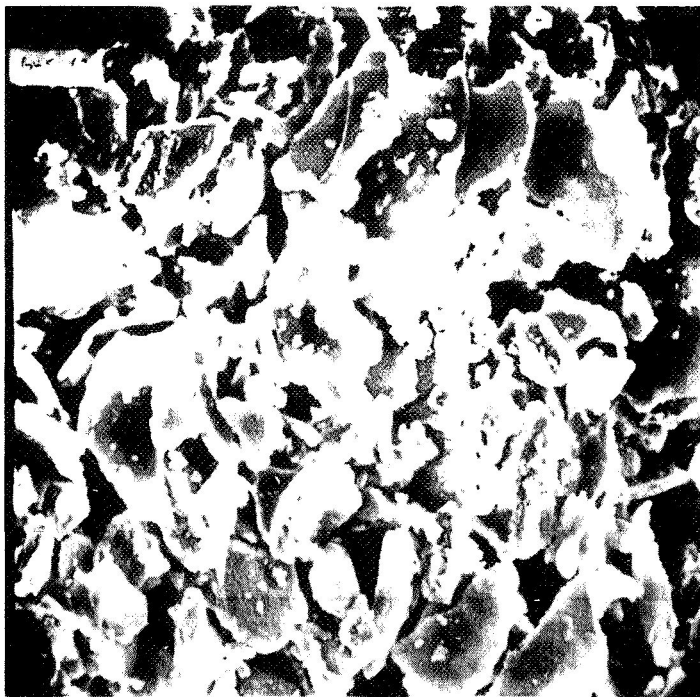


Figure 38. SEM OF MELLER 1.0 μ -U (300X)



Figure 39. SEM OF MELLER 1.0 μ -U (3,000X)

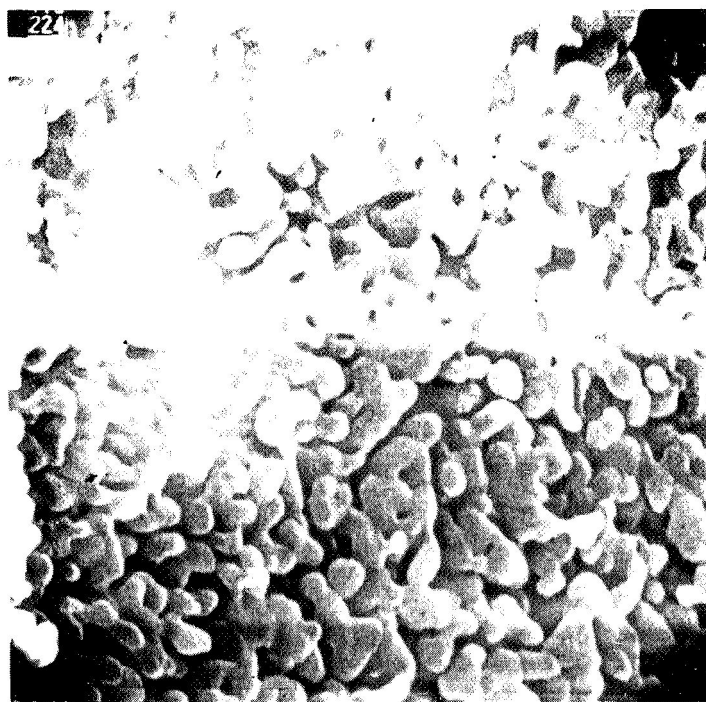


Figure 40. SEM OF MELLER 1.0 μ -U (10,000X)

The remarks made about M-1.0 apply equally as well to the spectra of M-3.0 in Figure 41. The SEM pix in Figures 42 and 43 are similar except that the aggregate sizes seem to be smaller in M-3.0. This may explain the slightly lesser reflectance in the 2.0-2.6 μ region of M-3.0 compared to that of M-1.0

At this point there is enough evidence to speculate that spectral reflectance correlates with three parameters associated with particle geometry, each of which affects spectral reflectance in a region roughly a decade wide around its median characteristic dimension. The smallest parameter is the discrete particle size; the largest is the aggregate size. In between these is the average void spacing. The effect of each overlaps the others, and, because of size distributions, their peak effects tend to be broad maxima rather than bell shaped maxima predicted from theory for monosized particles.

4. Group IV

In studying the spectral reflectances of paint films, we, of course, encountered more variables and parameters affecting the properties of the dry film than we did with binderless films.

Film thicknesses, however, are more easily controlled and measured. Figure 44 displays the reflectance spectra of unpigmented methyl methacrylate (DuPont's Elvacite 6011) films. The very high reflectance values in the visible region and the decreasing reflectance with increasing thickness deserve special note. Figure 45 shows that the latter is not due to absorption. In spraying this material the film entraps air which forms voids in the dry film. The thin films cure very quickly and the voids are locked in; the thick films take a longer time to cure, during which the air bubbles can escape. The point we wish to make is that the inclusion of stable air bubbles in a paint film strongly affects its reflectance. To study the effects of pigments in vehicles, therefore, precautions must be taken to prevent the formation of voids. For real paint systems where high reflectance

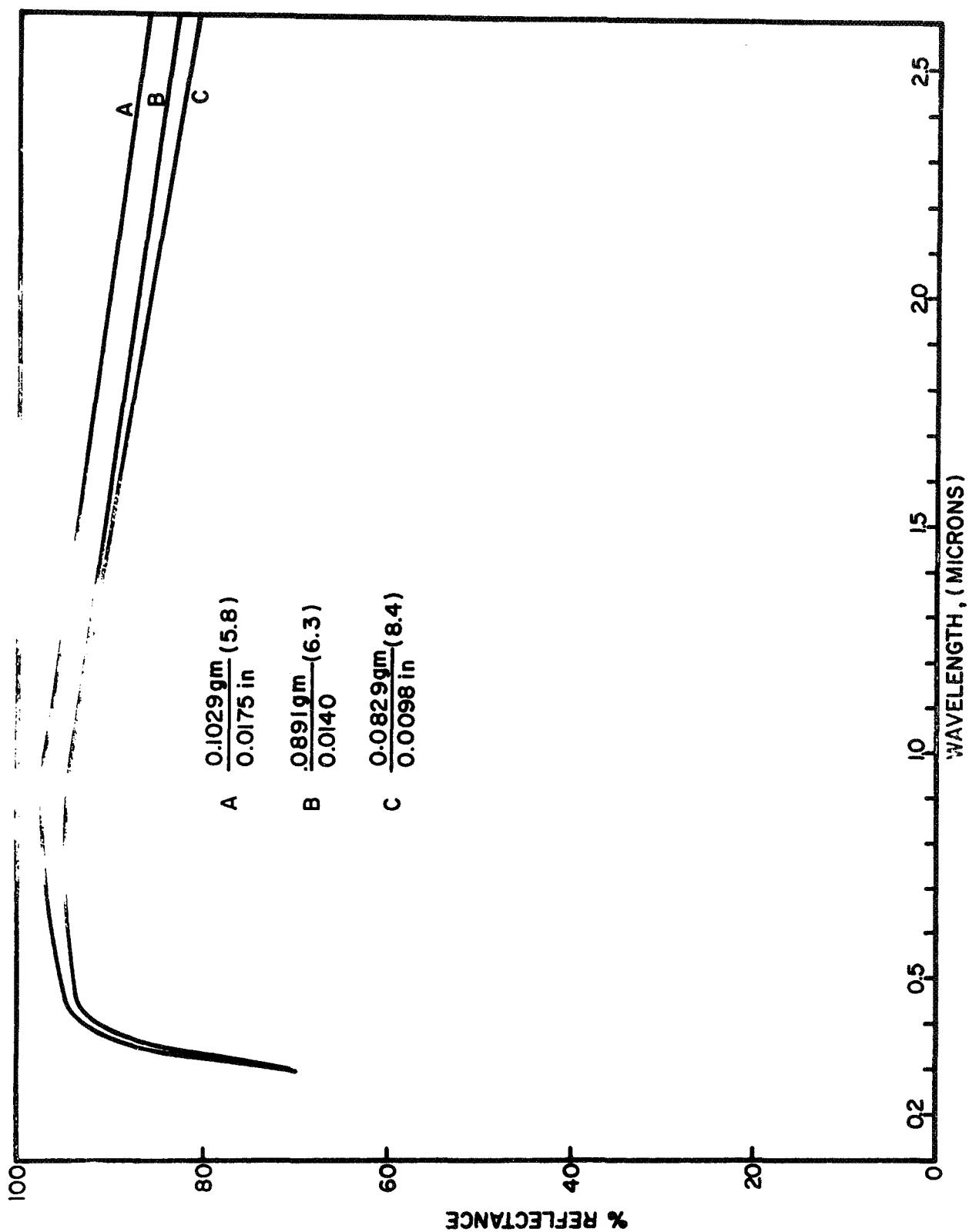


Figure 41. REFLECTANCE SPECTRA OF BINDERLESS MELLER 3.0 μ Al_2O_3

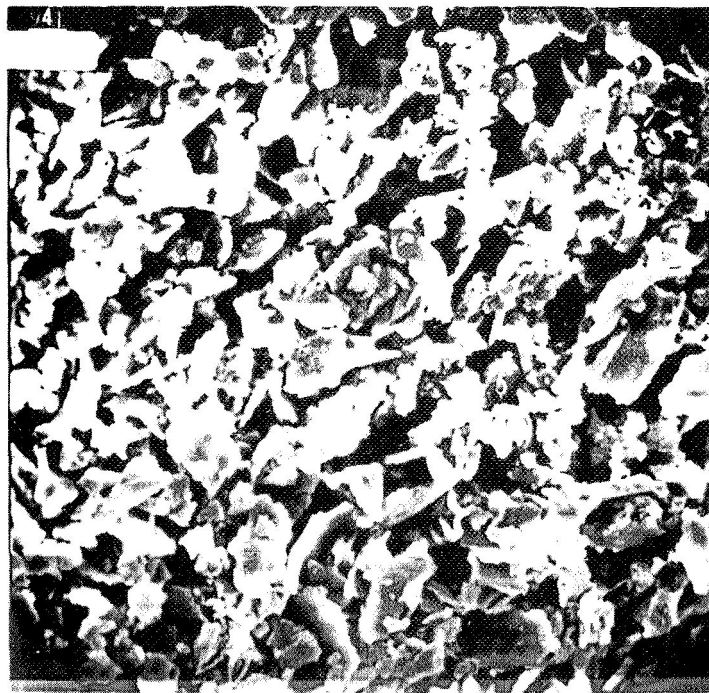


Figure 42. SEM OF MELLERS 3.0-U (300X)



Figure 43. SEM OF MELLERS 3.0-U (3,000X)

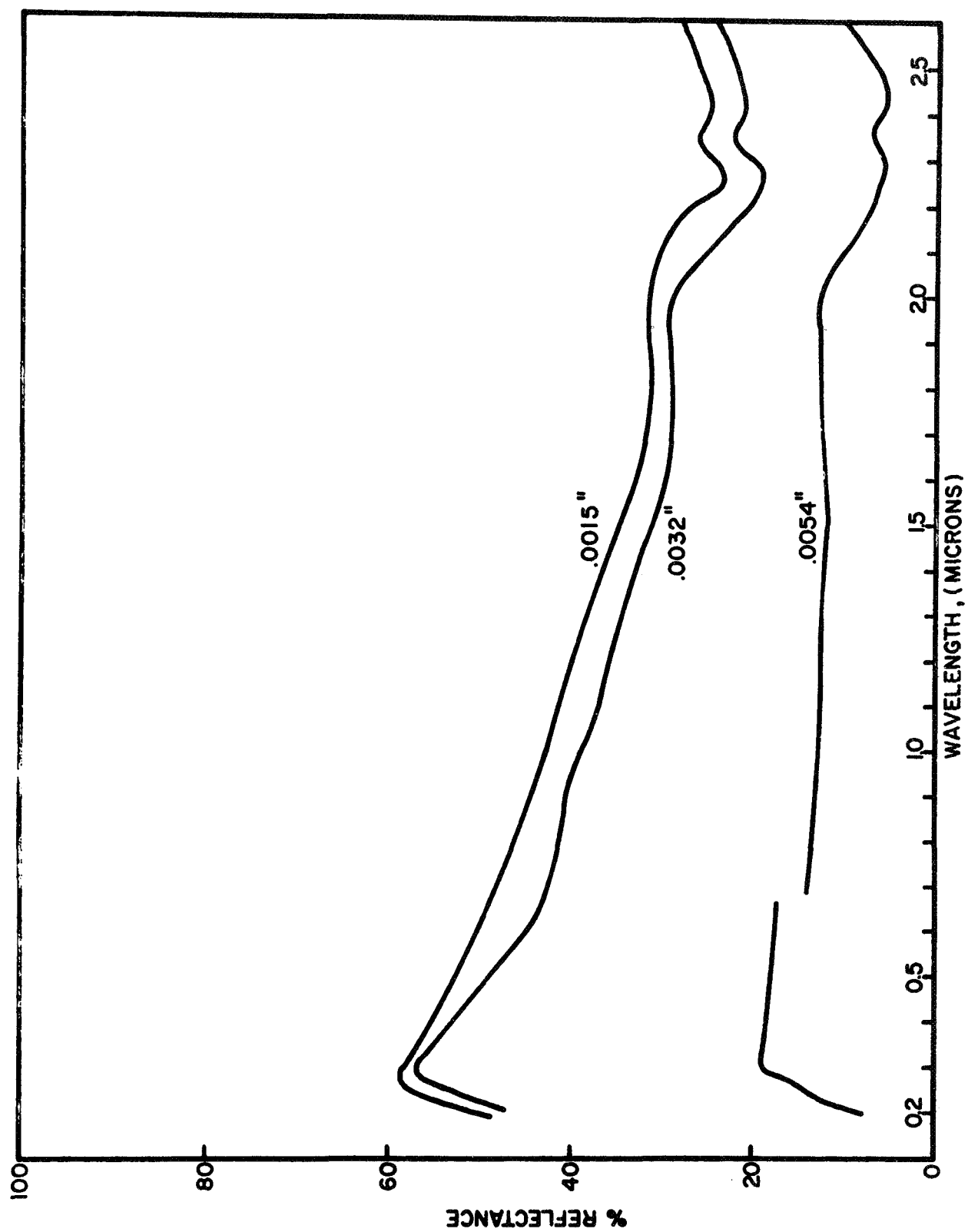


Figure 44. SPRAYED FILMS OF DUPONT ELVACITE 6011 REFLECTANCE VS. THICKNESS

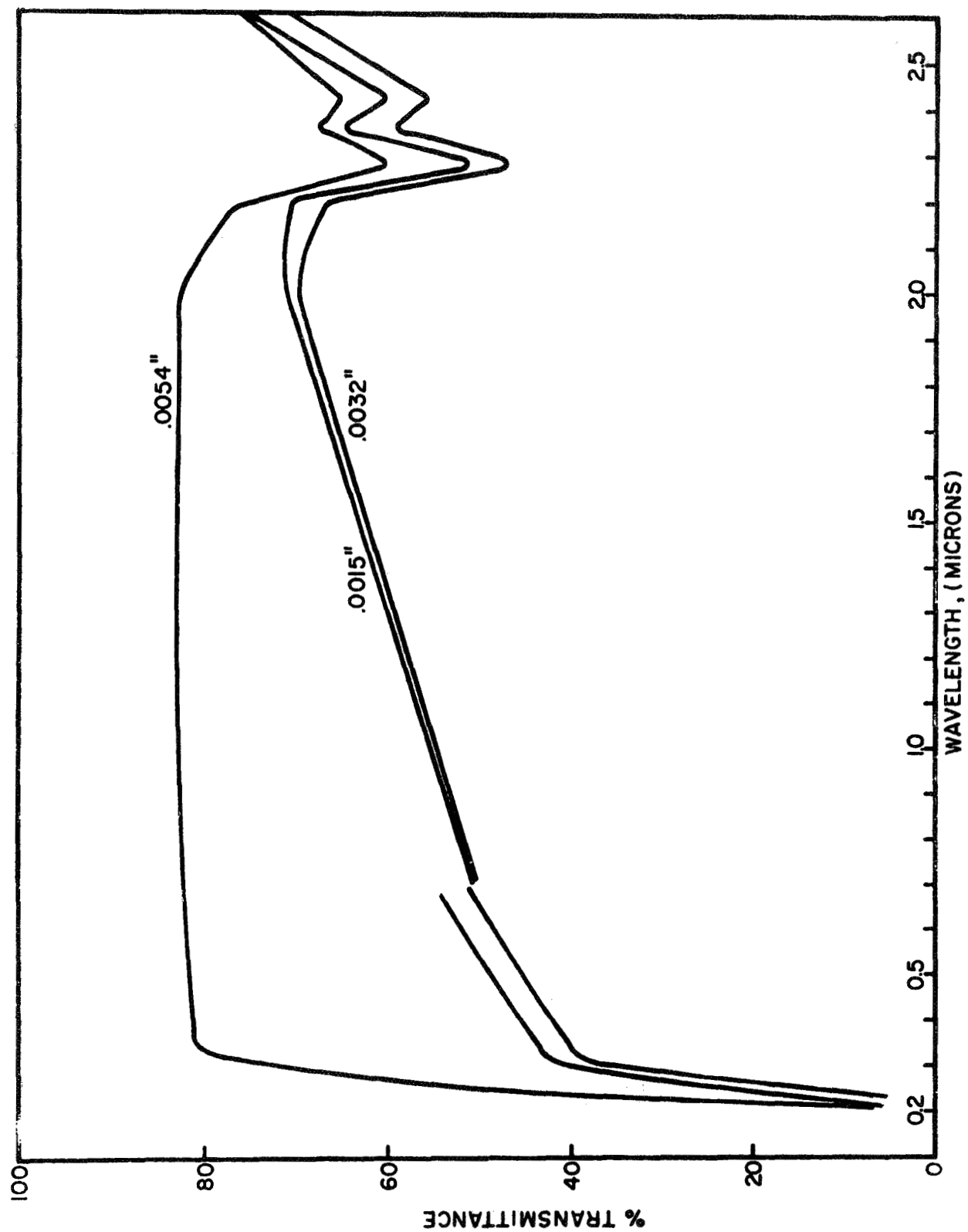


Figure 45. SPRAYED FILMS OF DUPONT ELVACITE 6011 TRANSMITTANCE VS. THICKNESS

is desirable, air turns out to be an excellent scattering center - it is environmentally stable and it is inexpensive.

Figure 46 presents transmittance spectra for several thicknesses of unpigmented methyl methacrylate (m-m) polymer films made by a doctor blade technique. These can be compared to the spectra in Figure 45. Interesting also is the comparison of the transmission spectra of m-m films pigmented to 30% PVC of M-3.0 with those of the films in Figure 46, in which the PVC of voids is unknown. Figure 47 shows another comparison of transmittance and reflectance spectra of m-m films; in this case, the films are relatively but comparably thick. Reflectance spectra shown in Figures 48 through 53 are from films pigmented to 30% PVC of Meller's Alumina pigments. Figure 49 shows R_λ spectra for doctored films of M-0.06 pigment and these can be compared with those from sprayed films in Figure 48. Spectra for M-0.3 pigmented films are in Figure 50; for M-1.0 in Figure 51; and M-3.0 in Figure 52. The effect of particle size does not appear as expected. The reflectance peaks do not occur at wavelengths related to their particle sizes; in fact, they all seem to peak between 0.4 and 0.5 μ . The steadily decreasing reflectance with increasing wavelength contrasts with the spectral reflectance behavior of binderless films. Several explanations are possible. The most likely is that the ball milling effectively broke up the aggregates and thereby decreased reflectance at long wavelengths. If the ratio of the indices of refraction of Al_2O_3 to m-m decrease with increasing wavelength, a corresponding decrease in spectral reflectance is also expected. The effect may be a combination of these. Figure 53 rules out the possibility of an increasing spectral absorptance.

The mismatch in the spectral curves at 0.7 μ results from the fact that the photomultiplier (0.2-0.7 μ) and lead sulfide (0.7-2.6 μ) detectors in the Beckman sphere have slightly different geometries with respect to the sample. The mismatch effect is intensified when the samples are transparent and highly specular.

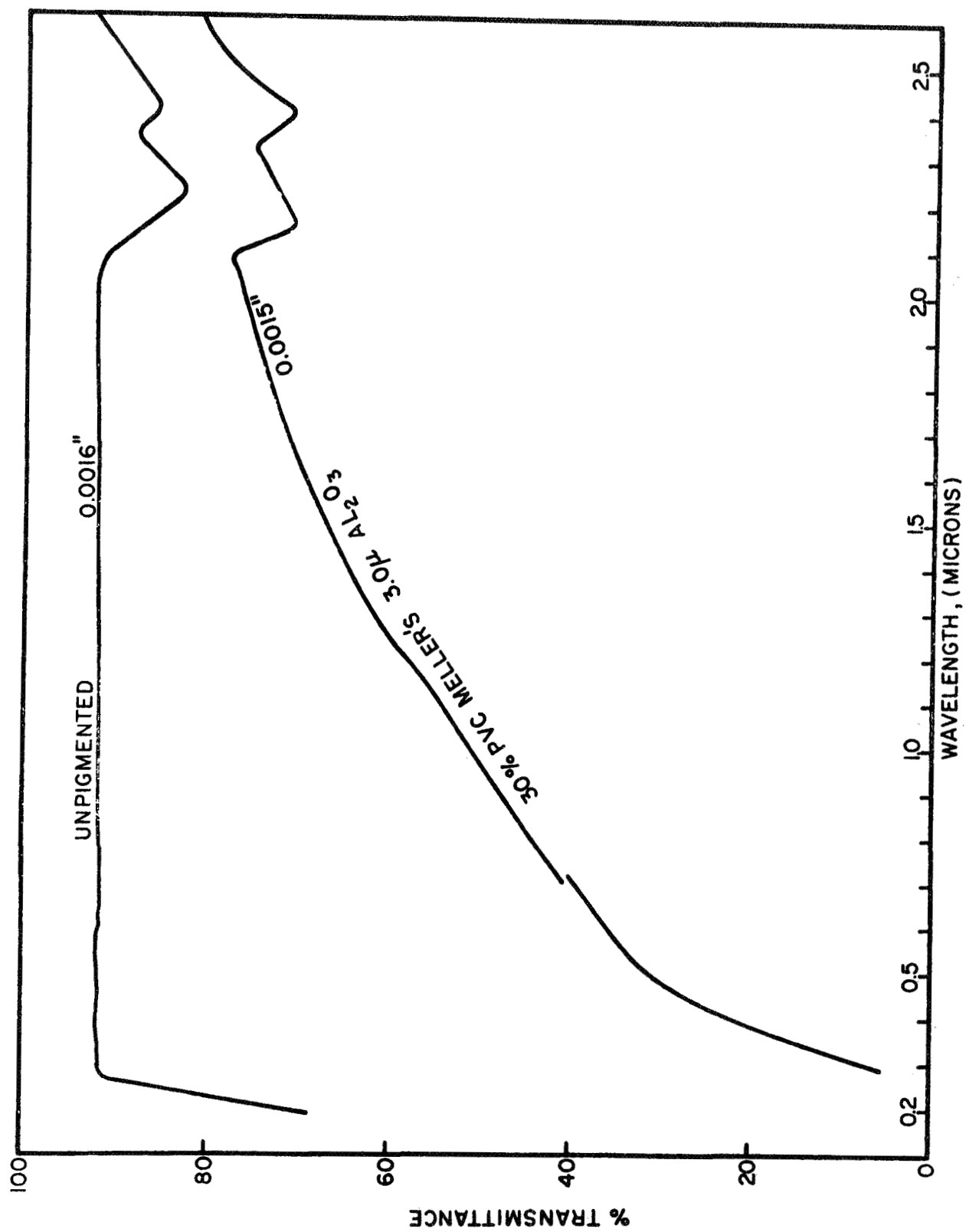


Figure 46. TRANSMITTANCE SPECTRA OF DOCTORED DUPONT ELVACITE FILMS
UNPIGMENTED VS. 30% PVC, MELLER 3.0μ AL₂O₃

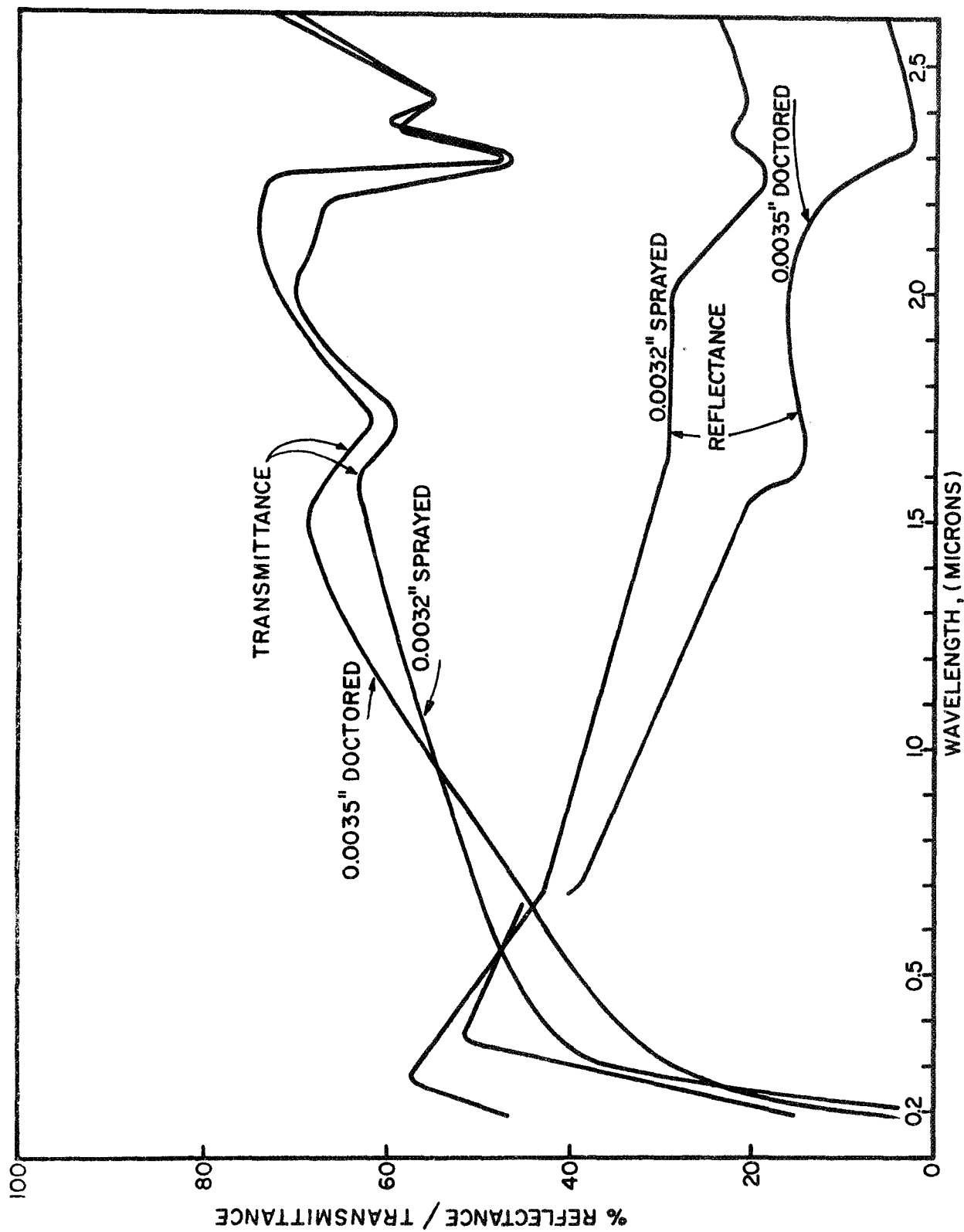


Figure 47. REFLECTANCE AND TRANSMITTANCE SPECTRA OF SPRAYED AND DOCTORED FILMS OF UNPIGMENTED DUPONT ELVACITE 6011

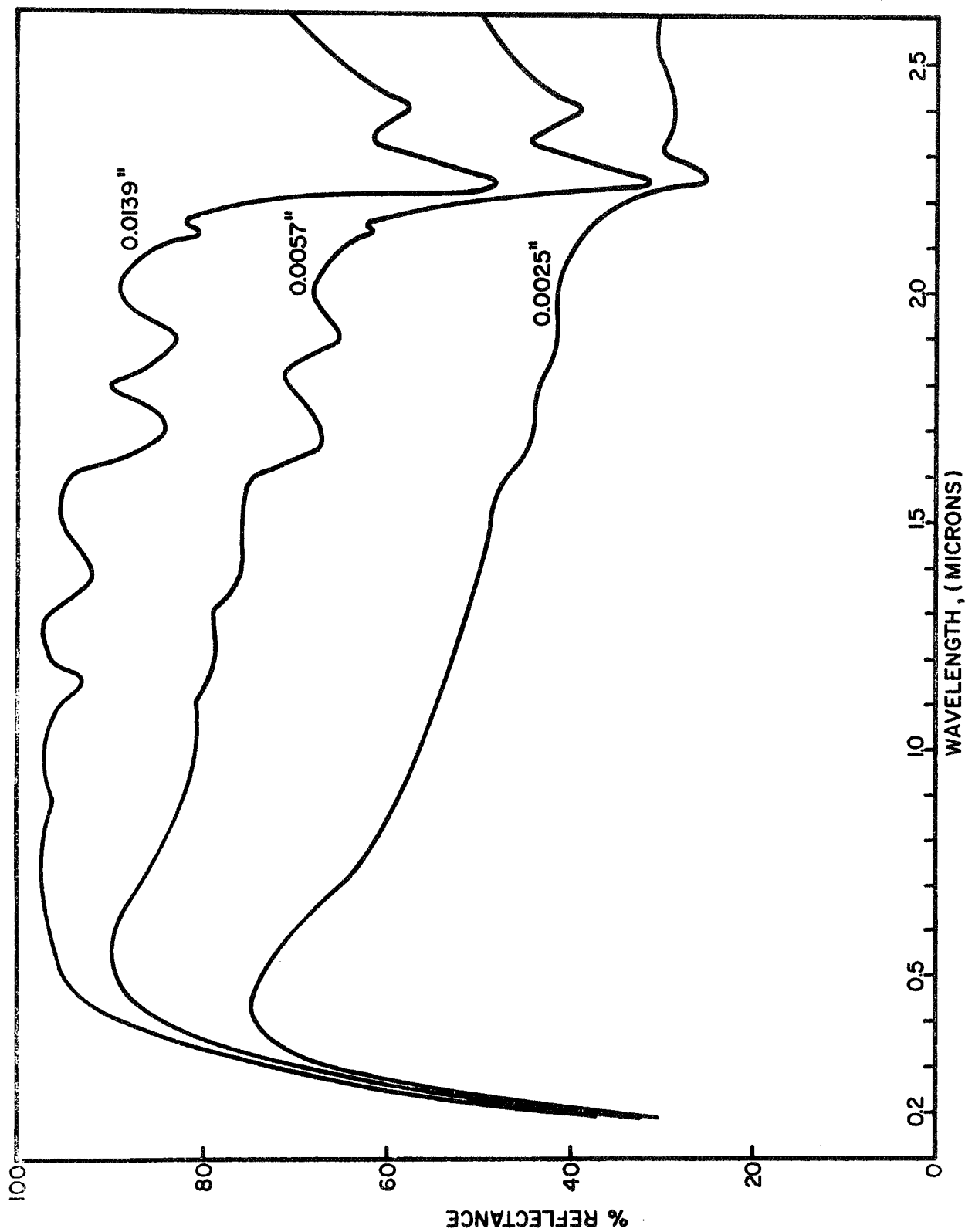


Figure 48. REFLECTANCE SPECTRA OF SPRAYED FILMS OF MELLER 0.06 μ Al_2O_3
AT 30% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

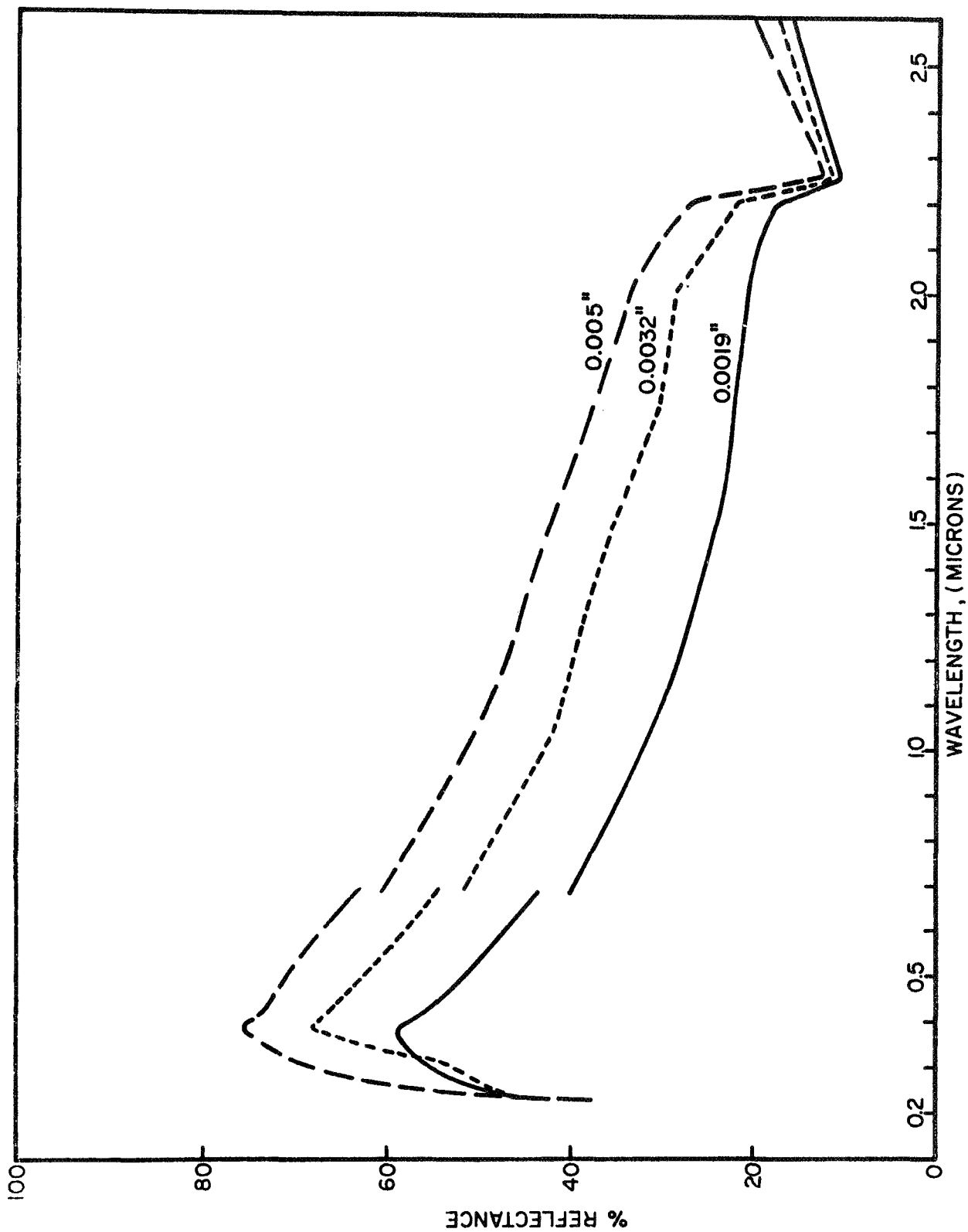


Figure 49. REFLECTANCE SPECTRA OF DOCTORED FILMS OF MELLER 0.06 μ Al_2O_3
AT 30% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

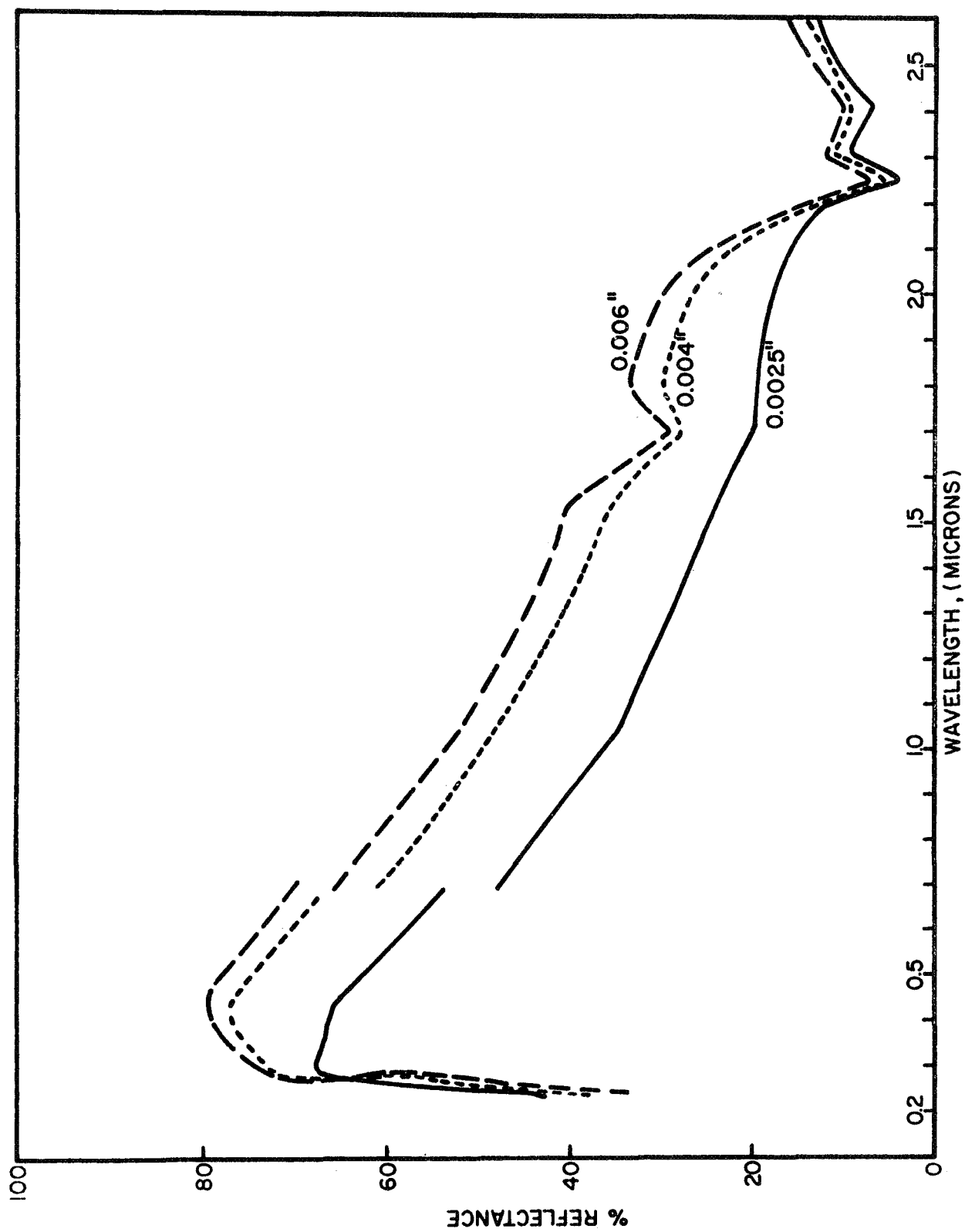


Figure 50. REFLECTANCE SPECTRA OF DOCTORED FILMS OF MELLER 0.3μ Al_2O_3
AT 30% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

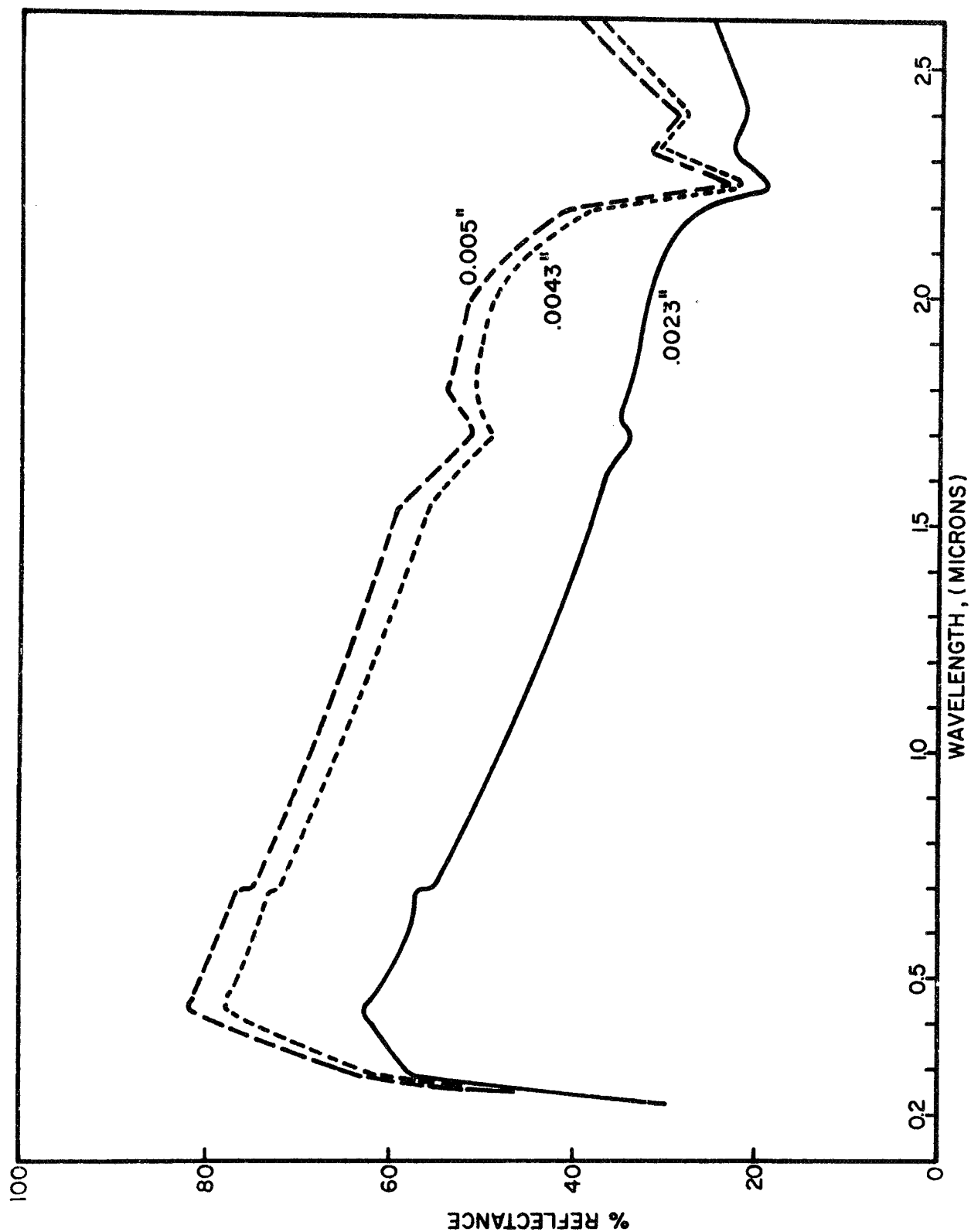


Figure 51. REFLECTANCE SPECTRA OF DOCTORED FILMS OF MELLER 1.0 μ Al_2O_3
AT 30% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

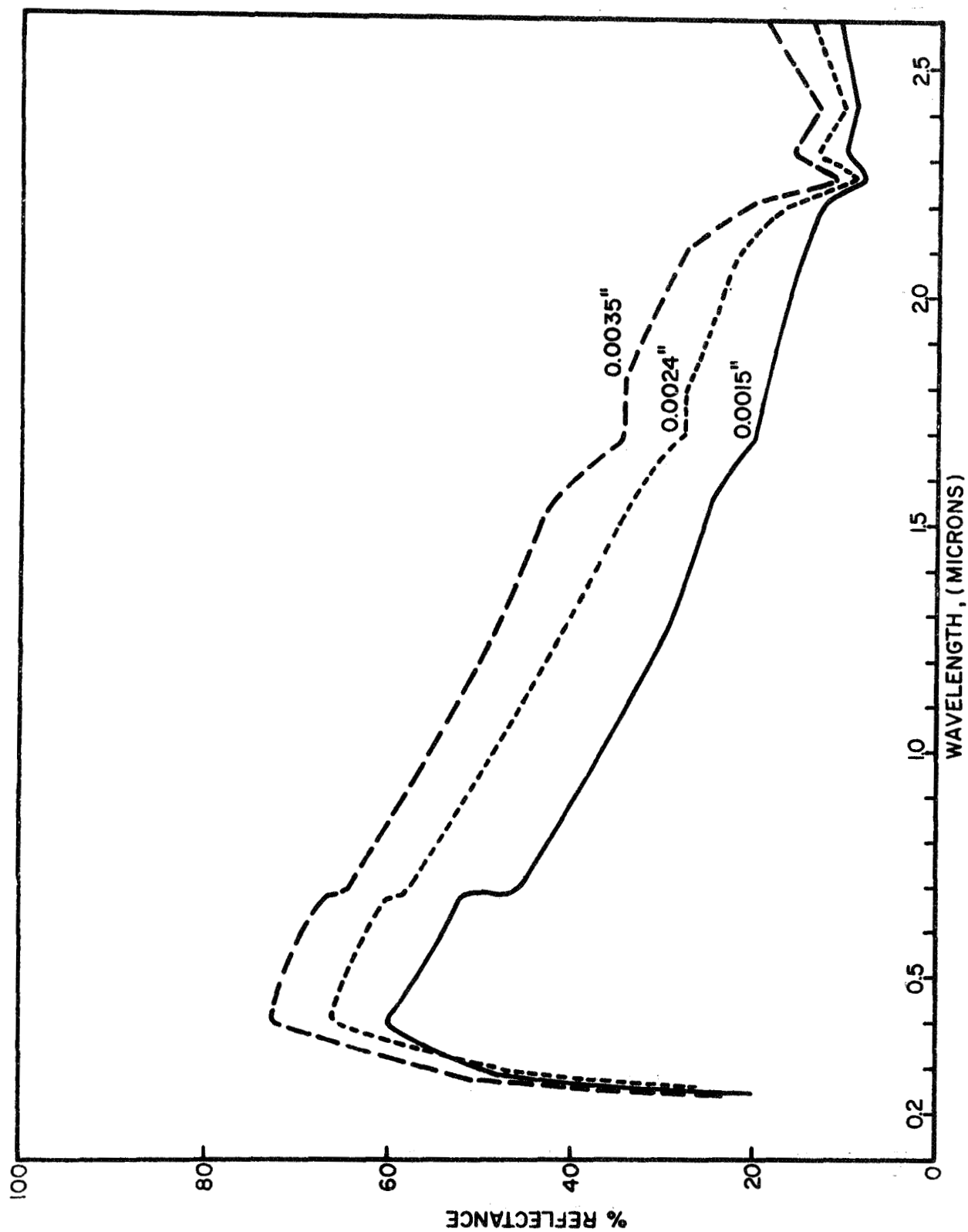


Figure 52. REFLECTANCE SPECTRA OF DOCTORED FILMS OF MELLER 3.0μ Al₂O₃
AT 30% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

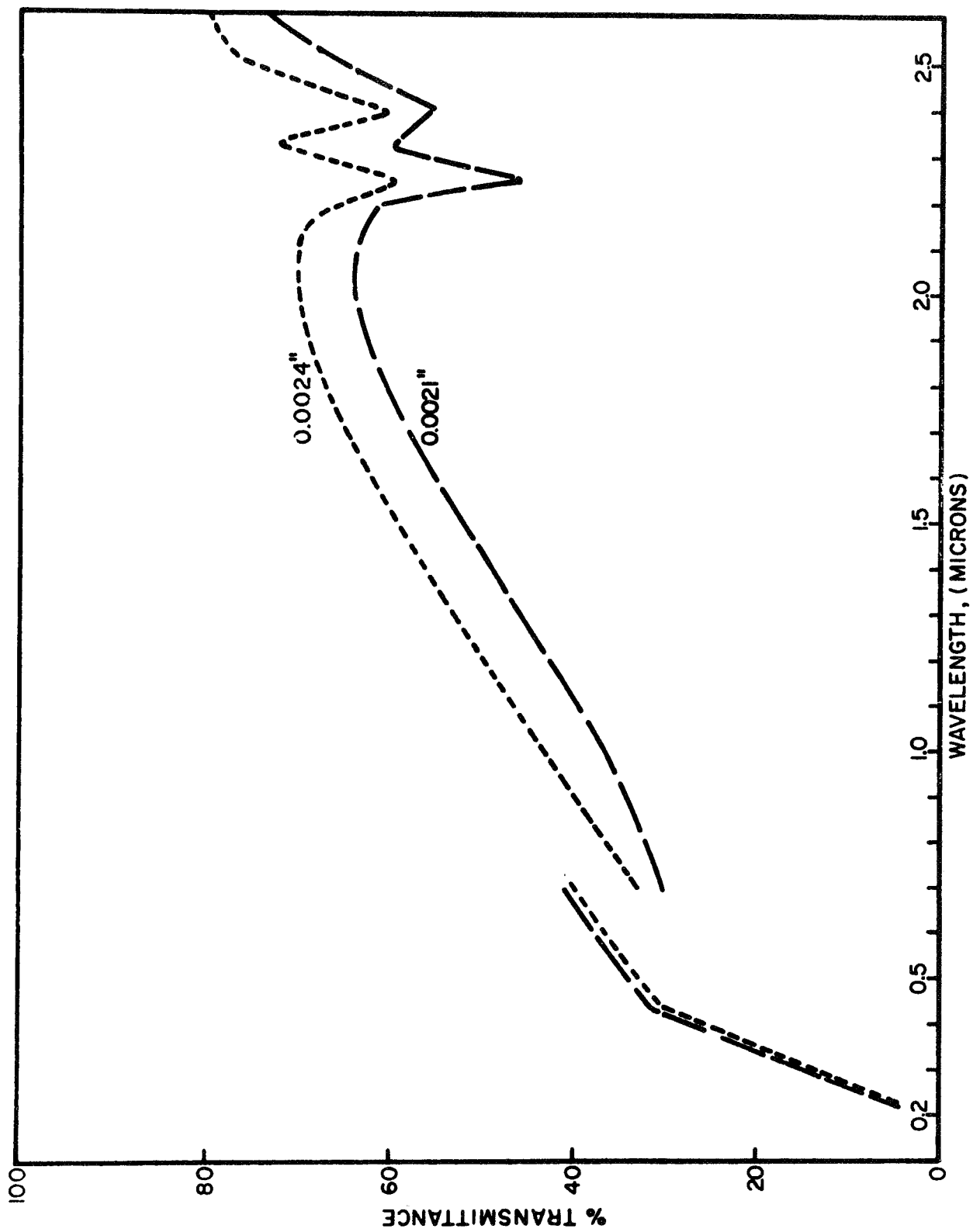


Figure 53. TRANSMITTANCE SPECTRA OF DOCTORED FILMS OF MELLER 3.0 μ Al₂O₃
AT 30% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

The advantage of the Beckman sphere is that both spectral reflectance and transmittance measurements can be made with the same sphere.

Figures 54, 55 and 56 show reflectance spectra of M-3.0 in m-m films pigmented to 0.1, 1.0 and 10% PVC. Figure 57 shows spectral reflectance of m-m films with different particle sizes; the films are of comparable thickness. The trends in the spectra are representative but their interpretation is difficult. The high reflectance of the 0.06μ film in the infrared is very puzzling. All of the paints were ball-milled under identical conditions for 7 hrs; they were put on and taken off the same roller mill at the same time. The films in each case were doctored to minimize air entrapment; yet it is not possible to prevent it completely during the milling process or in doctoring the films, and some void scattering may be present.

The effects of scattering on absorption in m-m have been investigated by calculating the extinction coefficients at a wavelength of 2.26μ . The latter is a natural absorption band in the methyl methacrylate. Table 5 lists the measured apparent densities of some of the films used. The true density of methyl methacrylate is 1.24 gm/cm^3 . At 30% PVC of alumina (density: 3.98 gm/cm^3), the film density should be about 2.06. The variations in film density are due to air entrapment. The density of the films increases with increasing thickness, because, as we noted earlier, the thicker films take longer to cure and the entrapped air has a better chance to escape. From these data, it would seem that doctor bladed films generally have higher densities and thus, less air voids. The doctored unpigmented films were completely transparent and clear; the sprayed, unpigmented films appeared milk white.

The extinction coefficients at $\lambda = 2.26$ of all the films were calculated from both the reflectance and transmittance spectra using the following formulae:

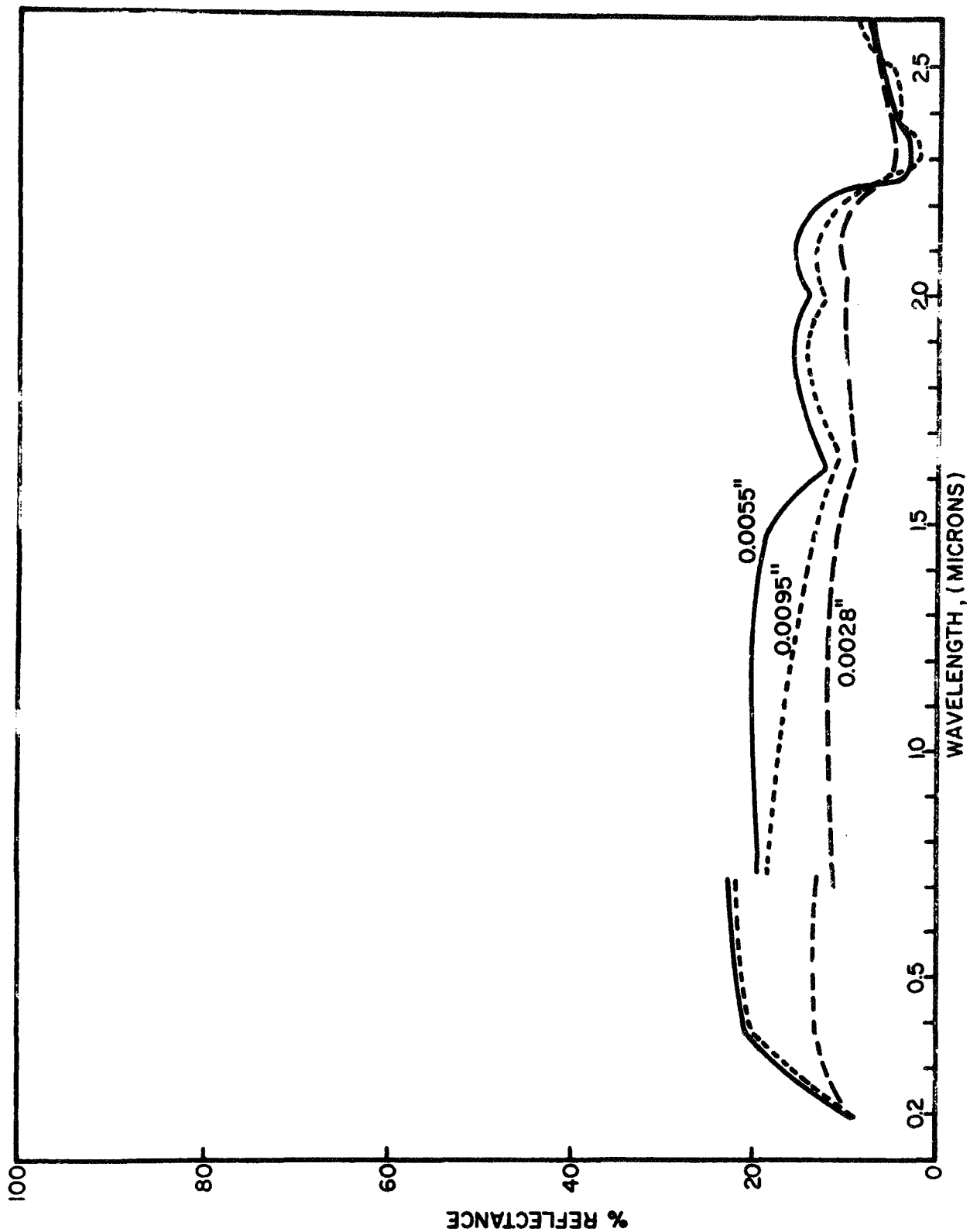


Figure 54. REFLECTANCE SPECTRA OF SPRAYED FILMS OF MELLER 3.0 μ Al_2O_3
AT 0.11% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

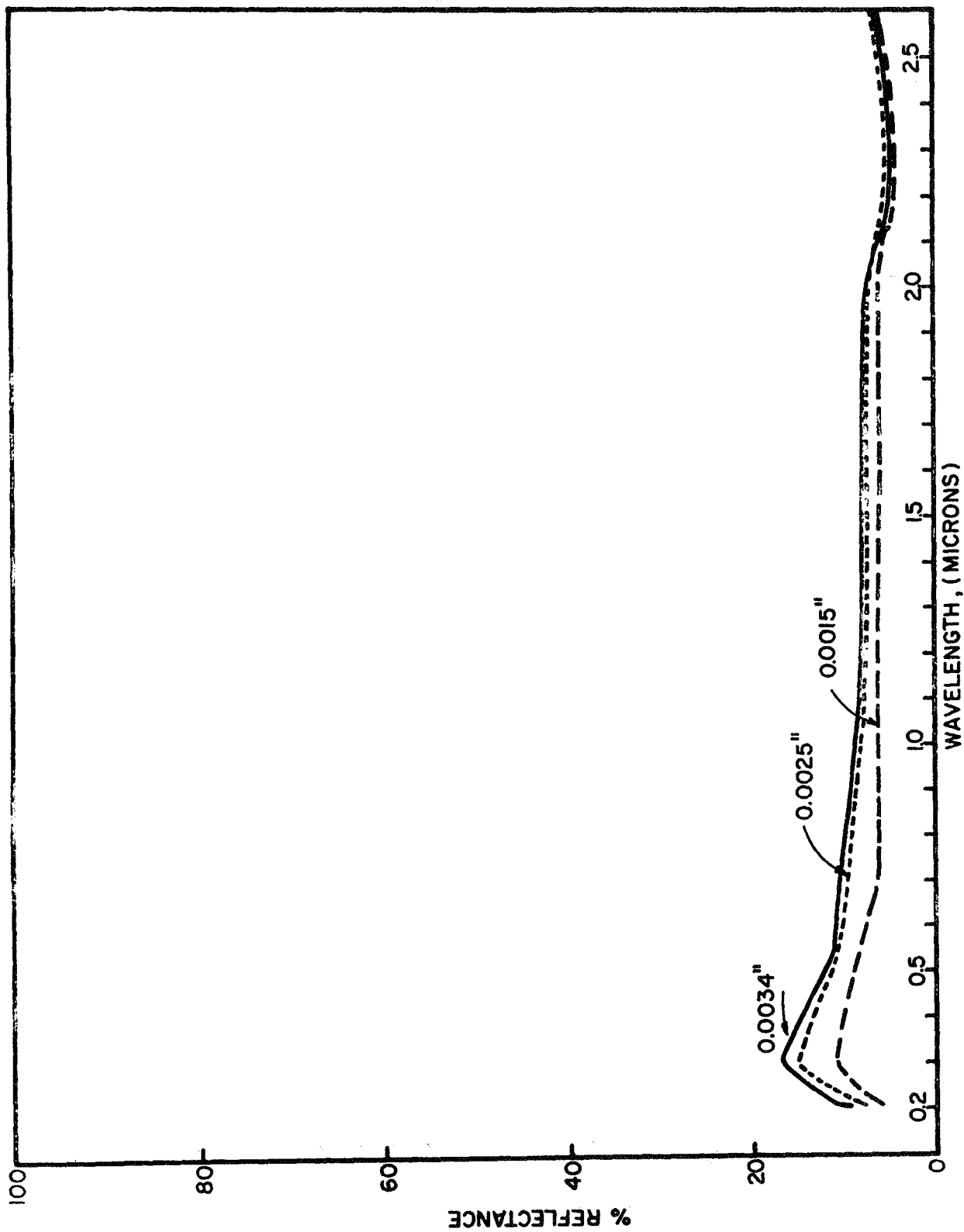


Figure 55. REFLECTANCE SPECTRA OF DOCTORED FILMS OF MELLER 3.0 μ Al_2O_3
AT 1% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

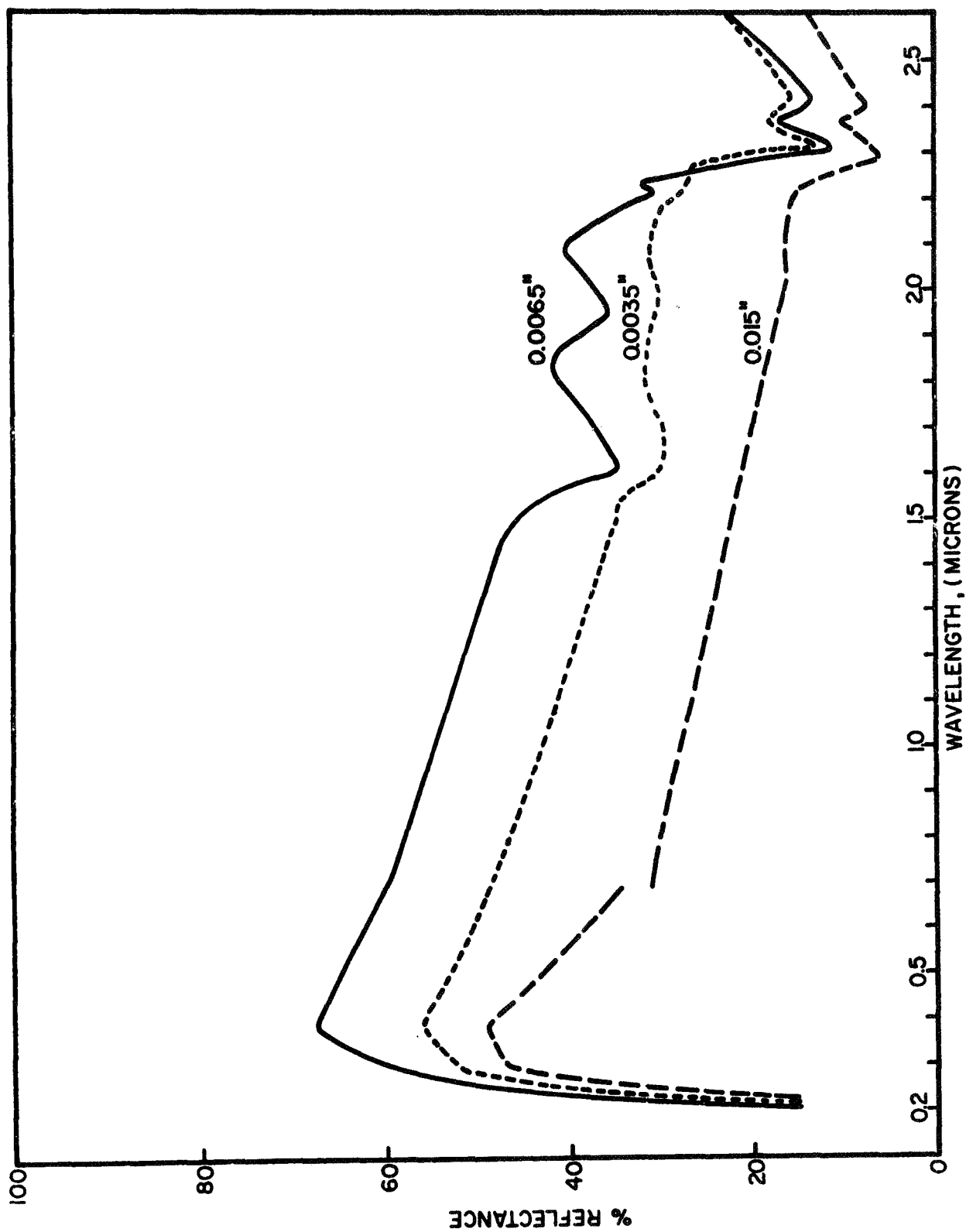


Figure 56. REFLECTANCE SPECTRA OF SPRAYED FILMS OF MELLER 3.0μ Al_2O_3
AT 10% PVC IN DUPONT ELVACITE 6011 VS. THICKNESS

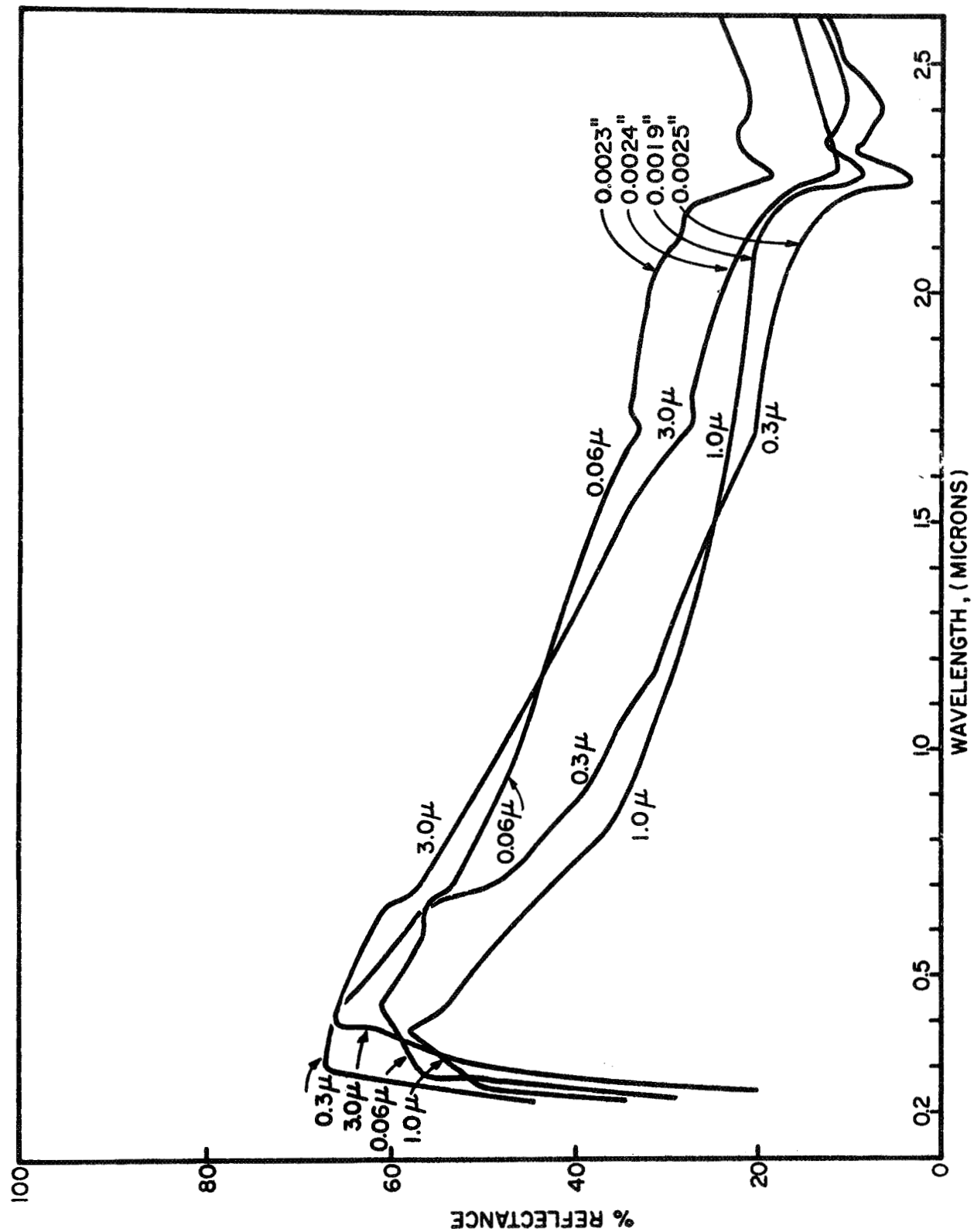


Figure 57. REFLECTANCE SPECTRA OF DOCTORED FILMS OF MELLER Al_2O_3
AT 30% PVC IN DUPONT ELVACITE 6011 VS. PARTICLE SIZE

Table 5

FILM DENSITIES* OF MELLER ALUMINA PIGMENTED ELVACITE

<u>Coating No.</u>	<u>Application Method</u>	<u>Thick. (in.)</u>	<u>Wt. (g)</u>	<u>g/cm³</u>
L-25 3.0 μ /30%	Spray	0.0021	0.0137	1.59
		0.004	0.240	1.46
		0.009	0.0603	1.63
L-25 3.0 /30%	Doctored	0.0015	0.0056	0.909
		0.0025	0.0121	1.18
		0.0038	0.019	1.22
L-27 1.0 μ /30%	Spray	0.0015	0.0063	1.02
		0.0027	0.0101	0.916
		0.0056	0.0300	1.35
L-27 1.0 μ /30%	Doctored	0.0023	0.0077	0.818
		0.004	0.0158	0.964
		0.006	0.0308	1.25
L-29 3.0 μ /1%	Spray	0.0012	0.0046	0.966
		0.0041	0.0172	1.02
		0.0075	0.0280	0.909
L-29 3.0 μ /1%	Doctored	0.0015	0.0050	0.811
		0.0025	0.0105	1.025
		0.0035	0.0150	1.043
Controls L-31	(no pigment) Spray	0.0018	0.0039	0.531
		0.003	0.0095	0.775
		0.0055	0.0160	0.708
Control L-31	(no pigment) Doctored	0.0007	0.0020	0.695
		0.0015	0.0041	0.666
		0.0020	0.0065	0.793
L-32 3.0 μ /10%	Spray	0.0015	0.0048	0.781
		0.0031	0.0103	0.806
		0.0063	0.0268	1.037
L-32 3.0 μ /10%	Doctored	0.0016	0.0056	0.854
		0.0023	0.0095	1.007
		0.0035	0.0176	1.225

* $\pm$ 20%

$$K_R = \frac{\ln(R_2/R_1)}{X_1 - X_2} \quad (54)$$

$$K_T = \frac{\ln(T_2/T_1)}{X_1 - X_2} \quad (55)$$

The parameters R, T and X are reflectance, transmittance and film thickness, respectively, with the numerical subscripts referring to different films. The derivation of these formulae removes the thickness-independent terms such as Fresnel reflectance, making K_R and K_T internal values. Note that in both equations, K has a positive value when the log term is negative and when X_2 is greater than X_1 . This is the usual case in transmittance: the thicker the film, the less the transmittance.

Tables 6a and 6b present the results of calculations of these coefficients. The trends are generally consistent. Because the negative values of K_R imply that an increase in thickness produces an increase in reflectance, the positive values are highly significant. There are two general trends to look for in these data - the effect of particle size in Table 6a and the effect of PVC in Table 6b. The trends are obvious; but, unfortunately, the effects of voids are also evident. The average (or effective) particle size(s) of the voids being unknown makes an interpretation difficult. In Figure 58, we have plotted K_R and K_T vs the size parameter, $\alpha (= 2\pi d/\lambda)$ for both doctor and sprayed films. The transmittance extinction coefficients, K_T , contrast sharply: the spray curve appears to have a minimum where the doctor curve has a maximum. The K_R curves also exhibit some interesting behavior. If the doctor films have an optically insignificant void fraction, then the effect of voids on reflectance can be very substantial, at $\alpha = 0.5$ void scattering makes the difference between $K_R = 70 \text{ cm}^{-1}$ and $K_R = -15 \text{ cm}^{-1}$.

The role of voids must be regarded as extremely important. In Table 6b, note that the K_T values for unpigmented films are roughly a factor of two different. The ratio K_T (spray)/ K_T

Table 5a

EFFECTS OF PARTICLE SIZE ON REFLECTANCE AND TRANSMITTANCE EXTINCTION COEFFICIENTS, K_R AND K_T (in cm^{-1}) OF MELLER ALUMINA PIGMENTED FILMS OF DUPONT ELVACITE 6011 AT $\lambda = 2.26\mu$

	d_p	0.06μ	0.3μ	1.0μ	3.0μ
α_1^*		0.167	0.934	2.78	8.34
d_p^*		0.06	0.2	0.4	0.5
α_2^*		0.167	0.556	1.112	1.39
K_T (doctor)	30%	73.3	94.5	113.5	85.2
K_T (spray)	30%	208	146	113	134
K_R (doctor)	30%	14.6	78.3	- 28.2	-49.0
K_R (spray)	30%	-22	-13.4	- 32.1	-36.3

Table 5b

EFFECTS OF PVC ON REFLECTANCE AND TRANSMITTANCE EXTINCTION COEFFICIENTS, K_R AND K_T (in cm^{-1}) OF MELLER ALUMINA PIGMENTED FILMS OF DUPONT ELVACITE 6011 AT $\lambda = 2.26\mu$, $d_p = 3.0\mu$

PVC	K_T (doctor)	K_T (spray)	K_R (doctor)	K_R (spray)
0 (L-31)	46.4	23.8	---	138
0.11 (L-30)	46.6	38.0	---	-28.7
1.0 (L-29)	56.4	76.5	---	-87.1
10.0 (L-32)	101/112.2**	94.1/104.5	---	-41.5/-46.1
30.0	85.2/121.5	134/191.5	-49/-70	-36.3/-51.8

* $\alpha_2 = 2\pi d/\lambda$; α_1 is calculated using nominal particle size, d_p ; α_2 , using TEM estimates of discrete particle size, d_p .

** Value corrected by factor $(1-\text{PVC}/100)^{-1}$ is on right of slash.

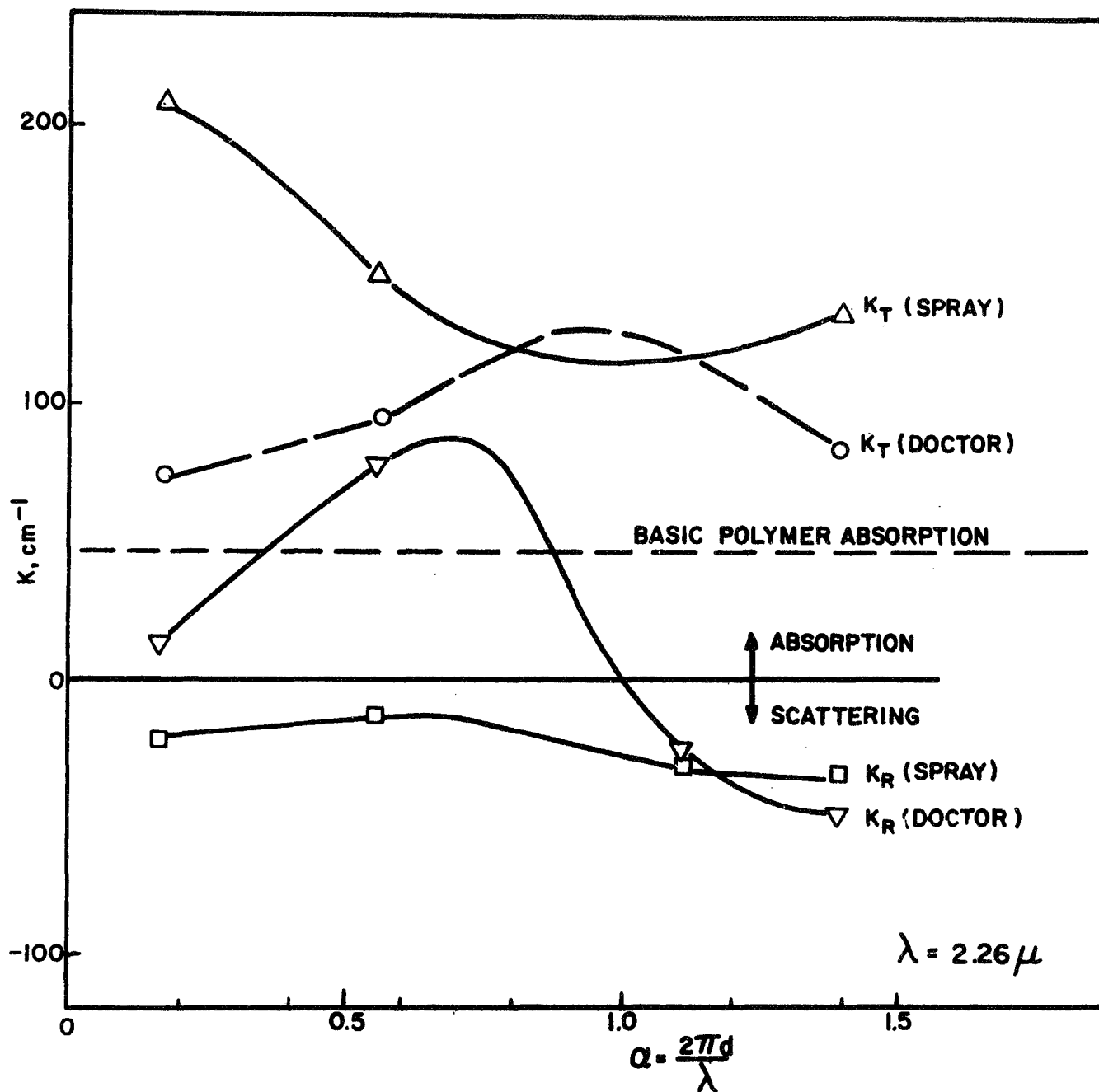


Figure 58. EXTINCTION COEFFICIENTS VS. SIZE PARAMETER FOR MELLER Al_2O_3 AT 30% PVC IN DUPONT ELVACITE 6011 (Methylmethacrylate) AT $\lambda = 2.26 \mu$

(doctor), however, increases strongly with PVC indicating that the effective absorption cross-section increases with particle scattering. Void-scattering reduces the absorption effect; the scattering due to pigments, increases it. These are very important conclusions, which we feel should be confirmed by further experiments. They follow from analyses of the data in Tables 6a and 6b and in Figure 58. Although attention was directed to the K_T values in Table 6b, the ratio of K_T (spray)/ K_T (doctor), as can be seen in Table 6a always exceeds unity, except for the 1.0μ particles.

A set of data similar to those in Tables 6a and 6b were obtained for $\lambda = 1.05\mu$. This wavelength was chosen because there is very little absorption in this region. Tables 7a and 7b present these data, which are shown also in graphical form in Figure 59. The unpigmented films show that air voids actually increase transmittance and decrease reflectance. This situation is reversed, however, when pigment is added. The values of transmittance extinction coefficients exceed those of reflectance extinction coefficients at this wavelength also. With absorption absent, the ratio of K_T (spray)/ K_T (doctor) is at least two orders of magnitude higher. It changes sign and drops sharply, with the addition of pigment, however, to values nearly the same as those for $\lambda = 2.26$, a wavelength of strong absorption. In comparison of the data at $\lambda = 1.05\mu$ with those at $\lambda = 2.26\mu$, we assumed that all of the absorption is in the vehicle and none is due to the Al_2O_3 pigment. As long as the absorption in the m-m exceeds that in the Al_2O_3 , the comparison of data at $\lambda = 1.05\mu$ with those at $\lambda = 2.26\mu$ will be at least qualitatively correct.

The last of the spectra in this group are given in Figures 60 and 61. They are spectral reflectance curves of Meller pigments at 30% PVC and at 0.01% PVC, respectively, in G.E. RTV 602 silicone. Surprisingly, these spectra show spectral reflectance decreasing in the infrared with increasing particle size. Absorption in the 2.28μ band of the silicone, however, does increase with increasing particle size. This behavior does not resemble that of the

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Table 7a

EFFECTS OF PARTICLE SIZE ON REFLECTANCE AND TRANSMITTANCE EXTINCTION COEFFICIENTS, K_R AND K_T (in cm^{-1}) OF MELLER ALUMINA PIGMENTED FILMS OF DUPONT ELVACITE 6011 AT $\lambda_R = 1.05\mu$

	d_p	<u>0.06μ</u>	<u>0.3μ</u>	<u>1.0μ</u>	<u>3.0μ</u>
α_1^*		0.360	1.80	5.99	18.0
d_p^*		0.06	0.2	0.4	0.5
α_2^*		0.360	1.20	2.39	2.99
K_T (doctor)	30%	98.0	67.6	87.9	112.5
K_T (spray)	30%	126.7	77.0	49.85	35.2
K_R (doctor)	30%	-61.1	-44.5	-51.8	-113.6
K_R (spray)	30%	-46.6	-43.9	-29.75	-16.6

Table 7b

EFFECTS OF PVC ON REFLECTANCE AND TRANSMITTANCE EXTINCTION COEFFICIENTS, K_R AND K_T (in cm^{-1}) OF MELLER ALUMINA PIGMENTED FILMS OF DUPONT ELVACITE 6011 AT $\lambda_T = 1.05\mu$, $d_p = 3.0\mu$

PVC	K_T (doctor)	K_T (spray)	K_R (doctor)	K_R (spray)
0 (L-31)	0.4	-34.6	---	108
0.11 (L-30)	3.0	5.6	-182	-31.9
1.0 (L-29)	12.6	20.1	-135	-79.4
10.0 (L-32)	76.0/84.5**	50.7/56.4	-161/-179	-57.3/-63.6
30.0	112.5/161	35.2/50.3	-114/-149	-16.6/-23.7

* $\alpha_e = 2\pi d/\lambda$; α_1 is calculated using nominal particle size, d_p , α_2 , using TEM estimates of discrete particle size, d_p .

** Value corrected by factor (1-PVC/100)⁻¹ is on right of slash.

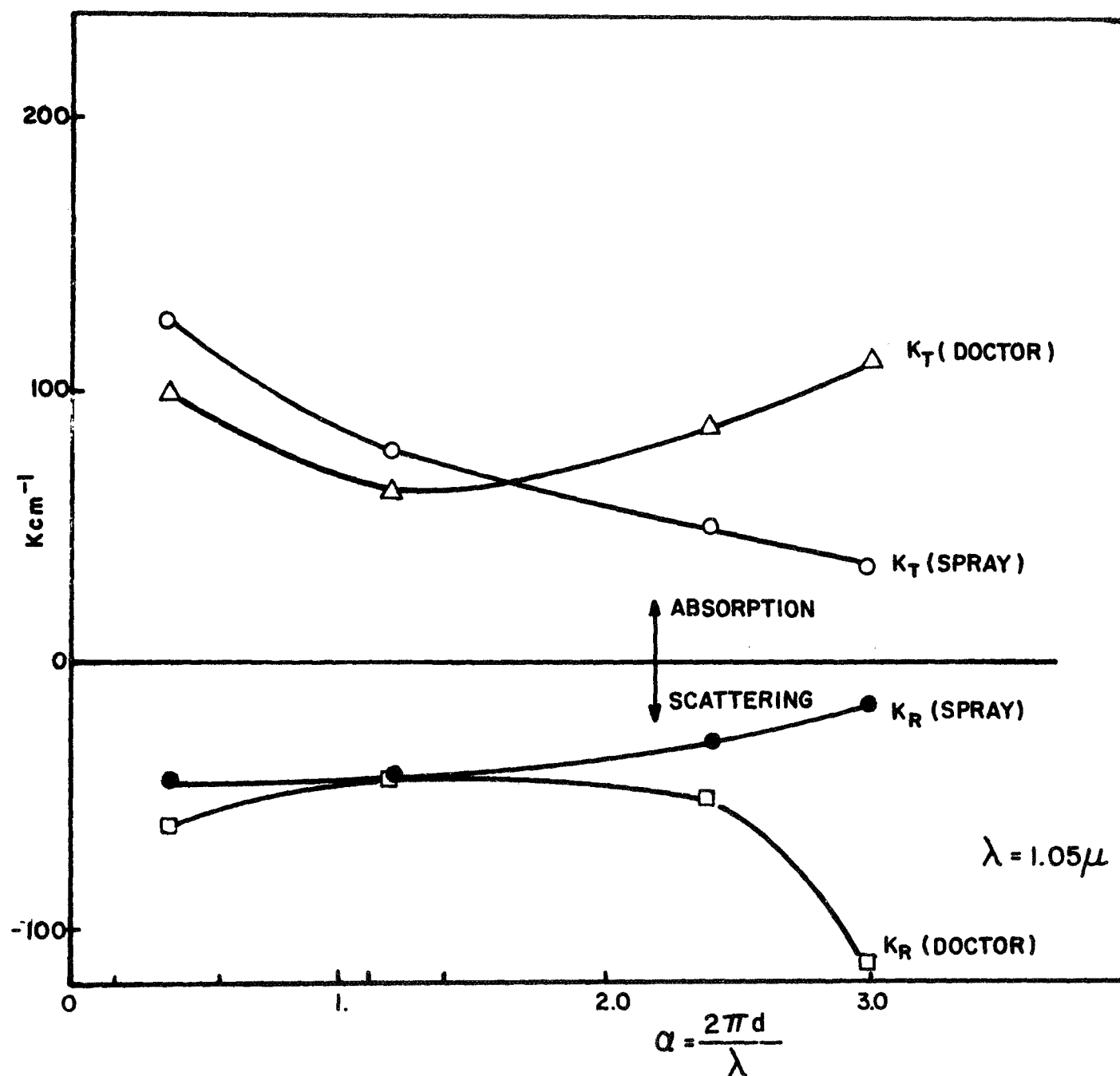


Figure 59. EXTINCTION COEFFICIENTS VS. SIZE PARAMETER FOR MELLER Al_2O_3 AT 30% PVC IN DUPONT ELVACITE 6011 (Methylmethacrylate) AT $\lambda = 1.05\mu$

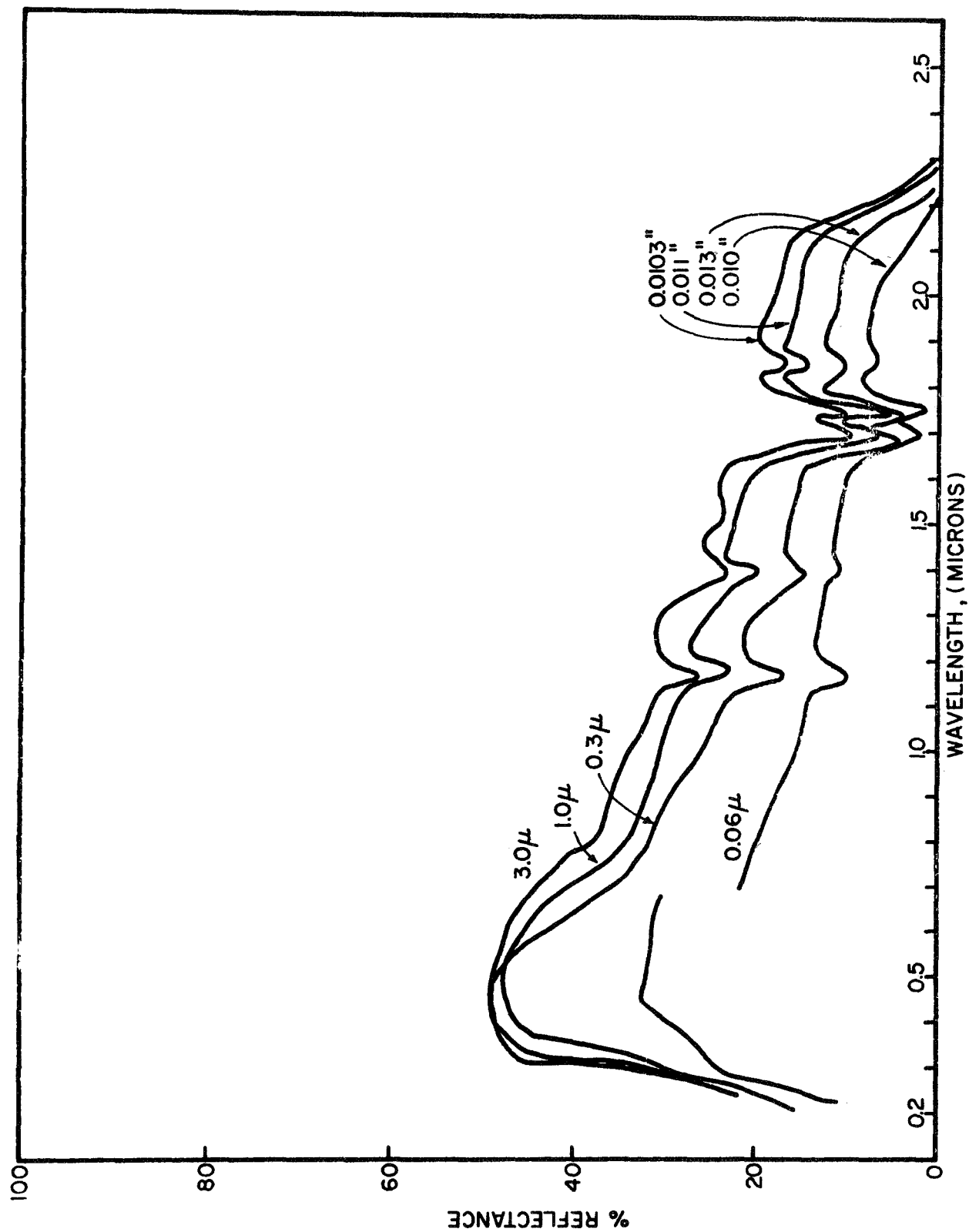


Figure 60. REFLECTANCE SPECTRA OF MELLER Al_2O_3 AT 30% PVC
IN G.E. RTV 602 VS. PARTICLE SIZE

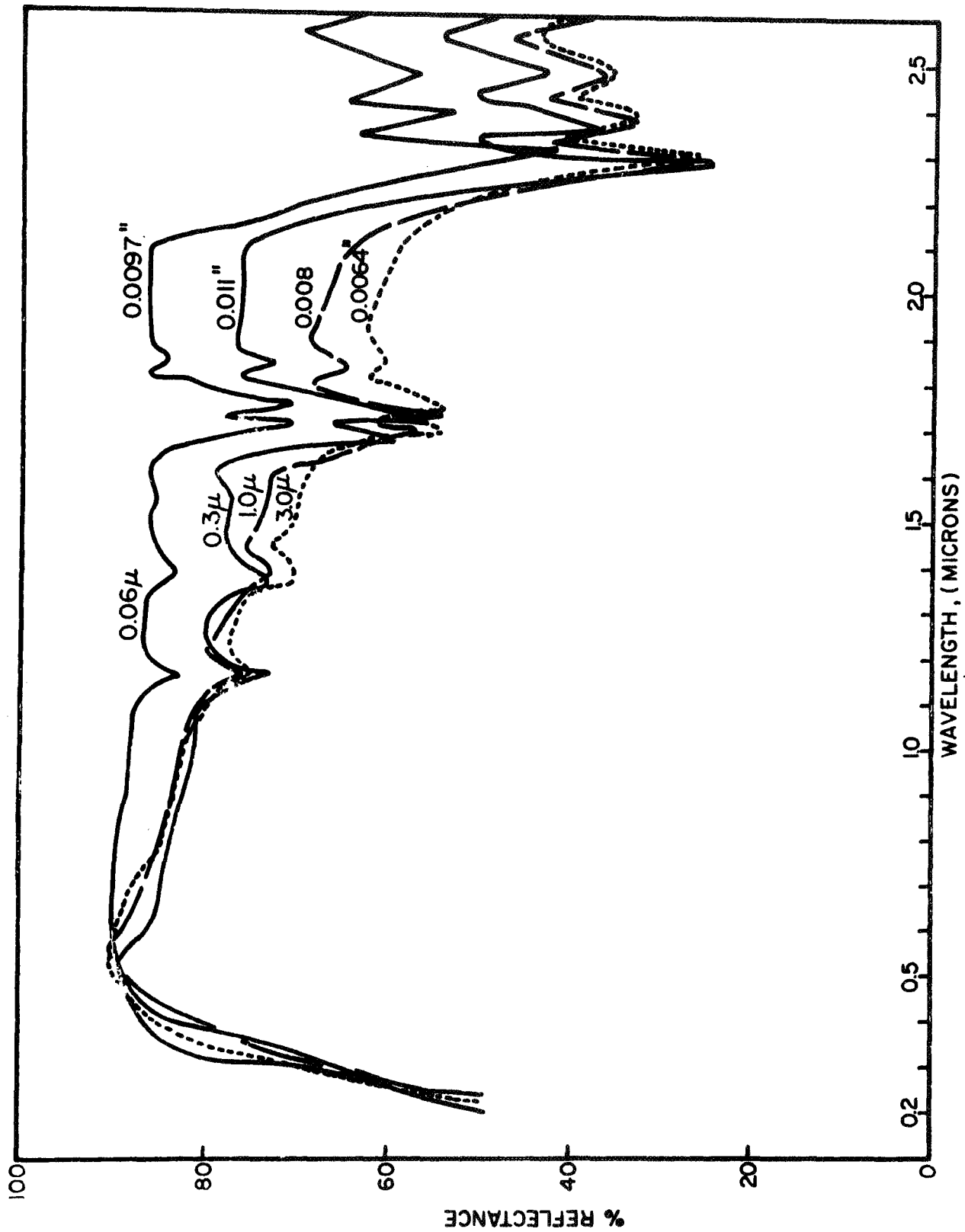


Figure 61. REFLECTANCE SPECTRA OF MELLER Al_2O_3 AT 0.01% PVC
IN G.E. RTV 602 VS. PARTICLE SIZE

Elvacite, but, since RTV 602 silicone does not readily sustain air voids, a comparison of the two vehicles is risky at best. The RTV films were not made in several thicknesses, nor were transmittance measurements made of them. Hence internal K constants cannot be calculated. The spectra of Meller's Al_2O_3 in RTV 602 are significant, however, in that the RTV 602 spectral reflectance vs particle size are the same as those for the Elvacite. The absence of air voids in the RTV films quite probably explains the fact that spectral reflectance decreases much more rapidly in RTV 602 than in Elvacite. Ball-milling in each case has undoubtedly broken up many of the aggregates, further decreasing the infrared reflectance.

5. Group V

Very careful and exact measurements were made on a final series of binderless coatings. The immediate objective in this series was to characterize the particle properties at each stage in the preparation of binderless films. The original, "as-received" powders, the particles in aqueous slurries (5% PVC), the particles in the spray, and the binderless films resulting from them were all characterized. The samples to be studied in the SEM were prepared simultaneously and as identically as possible with those for reflectance measurements. The reflectance samples were first measured on the Beckman DK-2A, after which they were installed in the IRIF-II, irradiated to an ultraviolet exposure of 339 ESH, and finally, exposed to O_2 at a pressure of 625 mm Hg. The intent in this procedure was to associate spectral reflectance changes with particle size; from our previous work, however, it was obvious that parameters other than particle size would be involved. It was, therefore, important to have documentation of the particle characterization at each preparation step. First, we characterized a particular film in terms of the "as-received" properties of the powder. Since these are modified in the spraying process, it became important to know the characterization change at each step and how it correlates with the original characterization. Second,

we wanted to know how reflectance degradation spectra depends upon the film structure in the binderless film.

The reflectance spectra of these highly characterized films have been shown in earlier sections, and it is worthwhile to note that the spectra in this section indicate much higher infrared spectral reflectances. The reason is that the earlier spectra were recorded in air and the IRIF-II "original" spectra have been taken under vacuum, and thus do not show the considerable water absorption the other binderless films do.

The characterization of binderless films, does not in any general way relate to that of the original powder. The TEM and SEM pix as well as other evidence show that the aggregates of some materials further agglomerate as a result of sonification, others break up. Associated with each reflectance specimen are a series of SEM pix of the coatings involved. These are presented along with each spectral reflectance curve. From the pix, one can determine which materials are further agglomerated and which are broken down by sonifying. The sonifying action essentially hurls one aggregate against another; if the collision results in a merger, or if it results in a breakdown, of one or both colliding aggregates, the net result is an increase in the size of aggregates, or an increase in the number of discrete particles, respectively. As would be expected the powders with the smaller discrete particle sizes apparently agglomerate faster than those with larger discrete particle sizes.

The breadth of the spectral reflectance spectra is determined by number distributions of particle, void and aggregate sizes, each with its own individual effect. How these factors will affect induced changes in reflectance depends in part upon the spectral region in which the reflectance degradation spectra is induced and upon the factor which is primarily responsible for reflectance in that region.

The reflectance degradation spectra of undispersed zinc sulfide in Figure 62 may be compared with that of dispersed zinc sulfide in Figure 63. Figures 64 and 65 are SEM pix at 3000X of these films; there is no obvious change in characterization as a result of dispersion. Ultraviolet damage in both films is mainly in the region 0.4-0.7 μ . The damage is slightly greater in the undispersed film, but there appears no essential difference in the shape of the spectra. Oxygen bleaching, a standard test at the end of IRIF-II tests, indicate little effect due to loss of absorbed oxygen.

A film of dispersed ZrO_2 , Figure 66, exhibits ultraviolet damage across the spectrum. This, we believe, is not a real effect. The drying effect in the IRIF vacuum caused the film to lose adhesion in places and the substrate to become partly exposed. More often the films lost cohesion and occasionally would lose a small amount of loose powder when being manipulated in and out of the integrating sphere. The film structures of undispersed and dispersed ZrO_2 can be seen, respectively, in Figures 67, 68 69 and 70. The dispersing action agglomerates the existing aggregates. The ultraviolet damage spectrum indicates a possible oxygen loss; but, without extensive testing, the spectra reveal no obvious particle size effects.

The Linde A film (dispersed) remained intact until the gas adsorbate test; therefore, the before and after ultraviolet spectra (Figure 71) are valid but the oxygen bleaching curve allows some of the substrate to be seen. The oxygen bleaching effect consequently is not real. The spectra in Figure 72 for dispersed Linde C look very much like those of dispersed Linde A. Their respective damage spectra are not different. The SEM pix reveal that the basic particle size remains unaffected by the dispersion treatment (3 mins in a sonifier). The film structure of Linde C, (undispersed, in Figure 73; and dispersed in Figure 74) now can be compared with that of Linde A, (undispersed, in Figure 75; and dispersed, in Figure 76). The physical differences between these

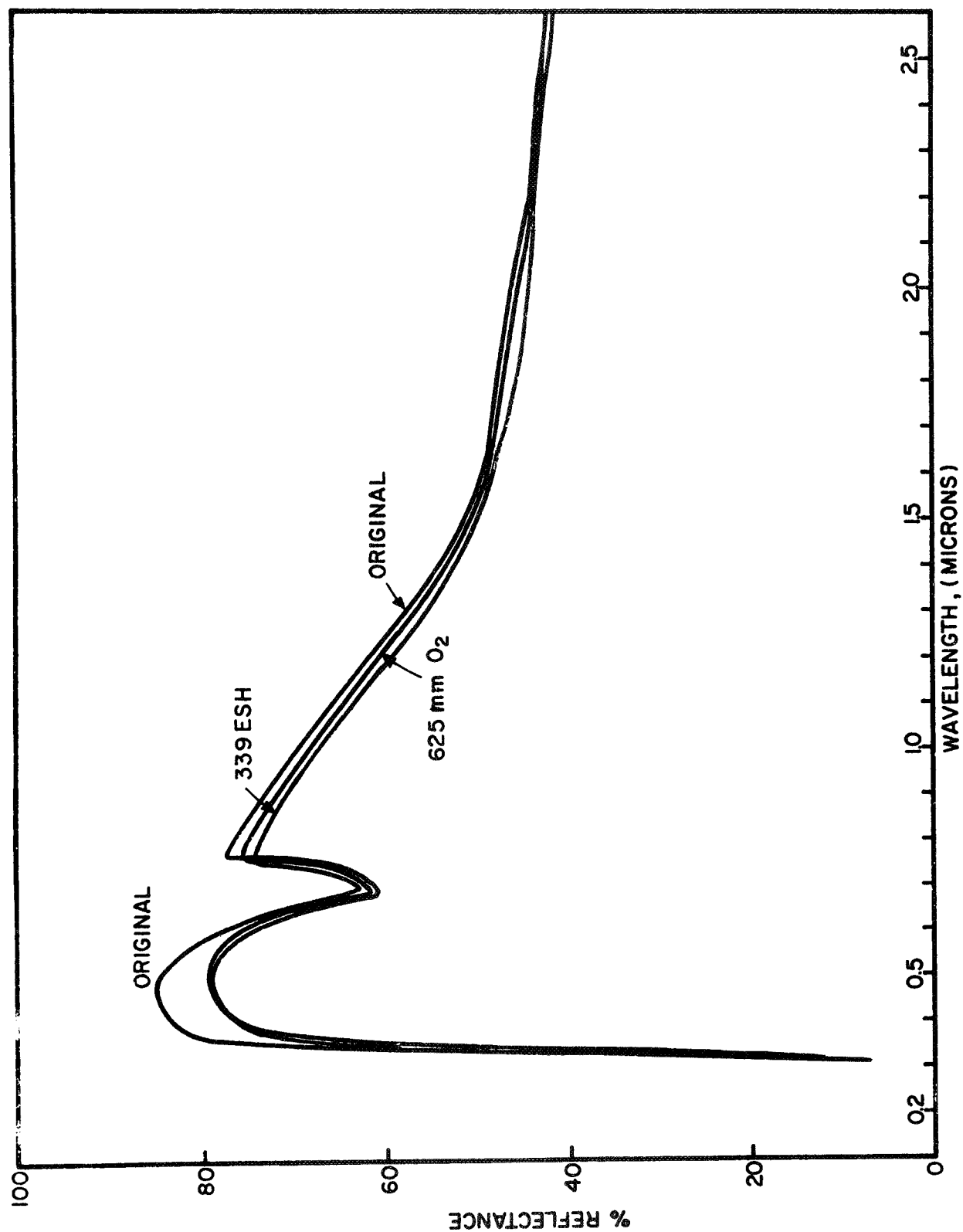


Figure 62. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS ZINC SULFIDE - UNDISPERSED

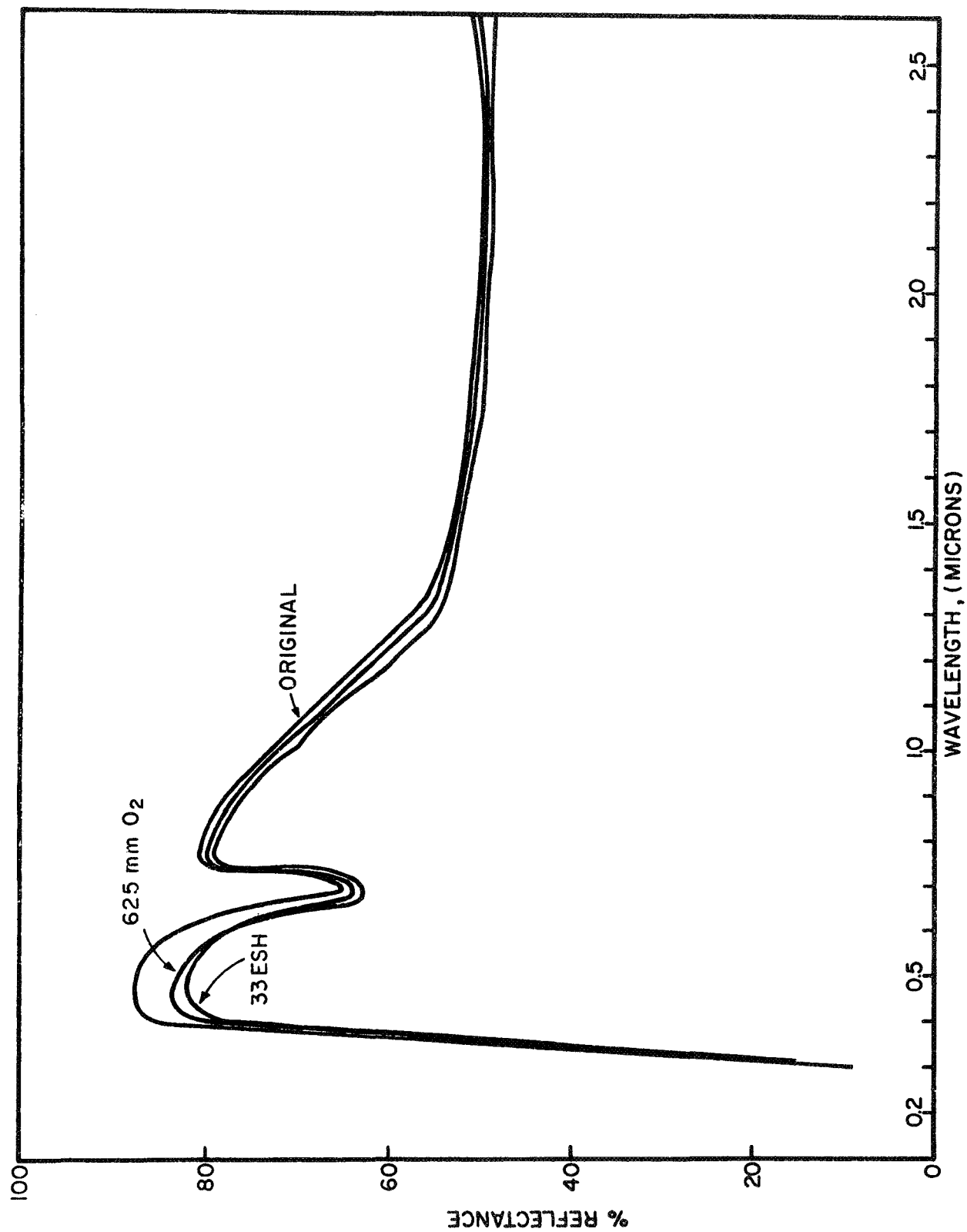


Figure 63. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS ZINC SULFIDE - DISPERSED



Figure 64. SEM OF ZnS-U BINDERLESS (3,000X)

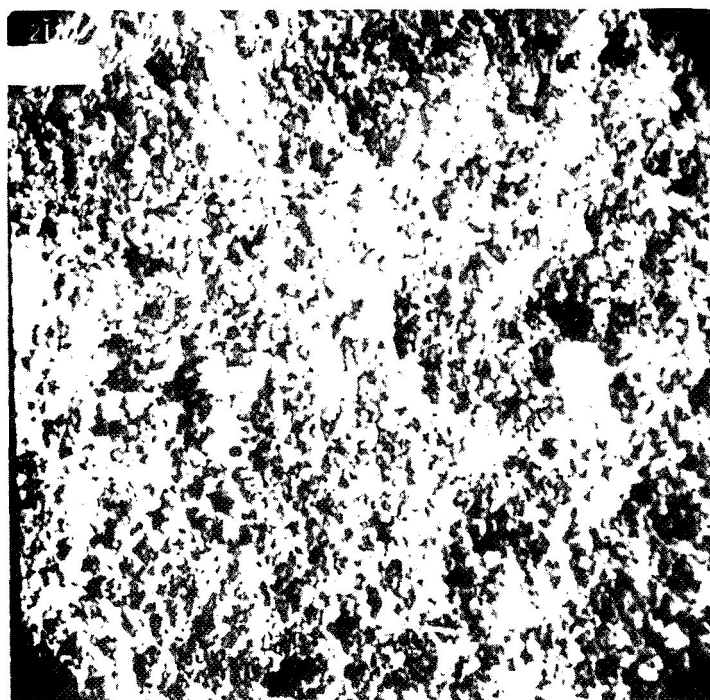


Figure 65. SEM OF ZnS-D BINDERLESS (3,000X)

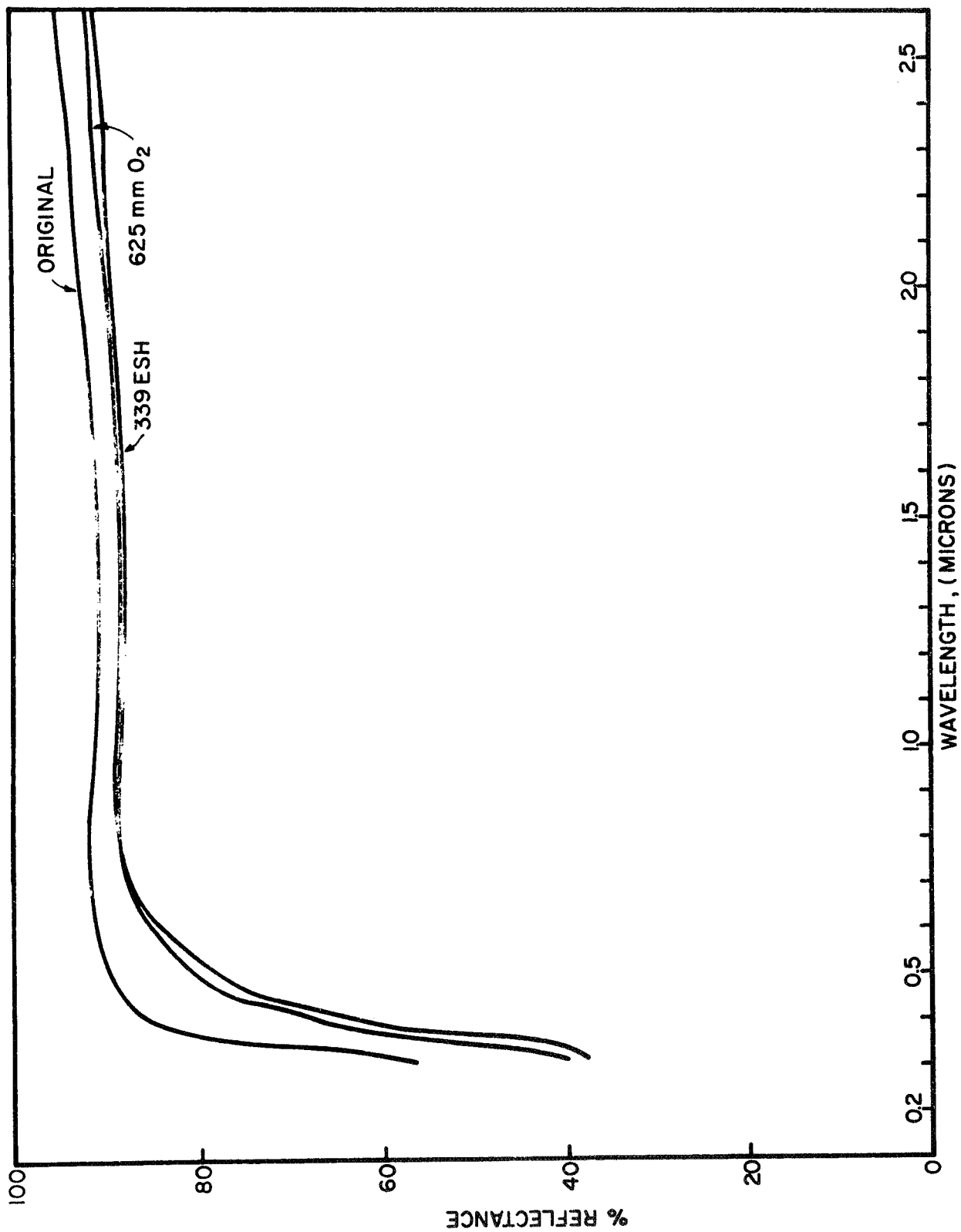


Figure 66. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS ZINC OXIDE - DISPERSED

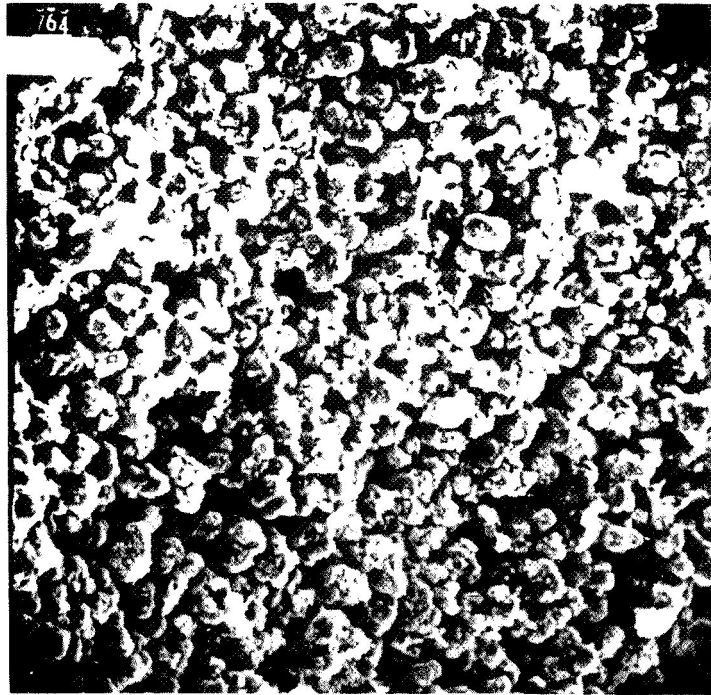


Figure 67. SEM OF ZrO₂-U (1,000X)

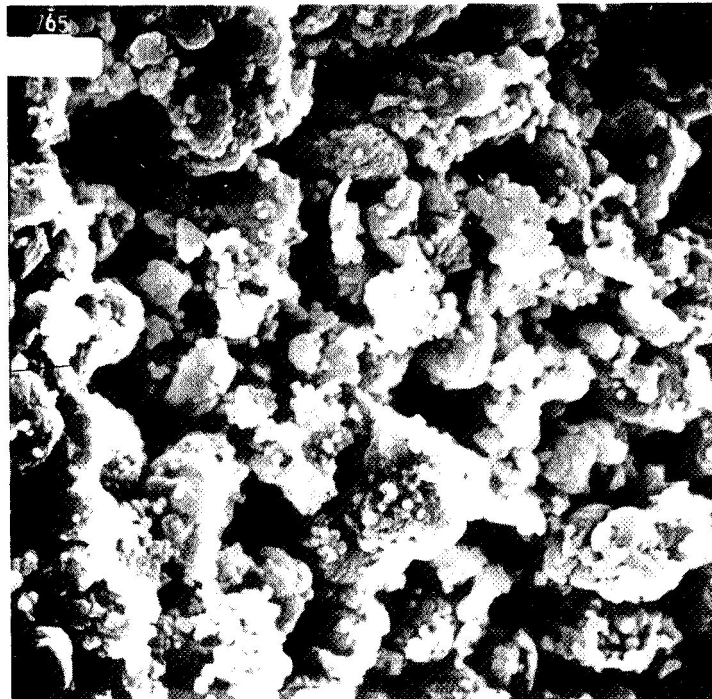


Figure 68. SEM of ZrO₂-U (3,000X)

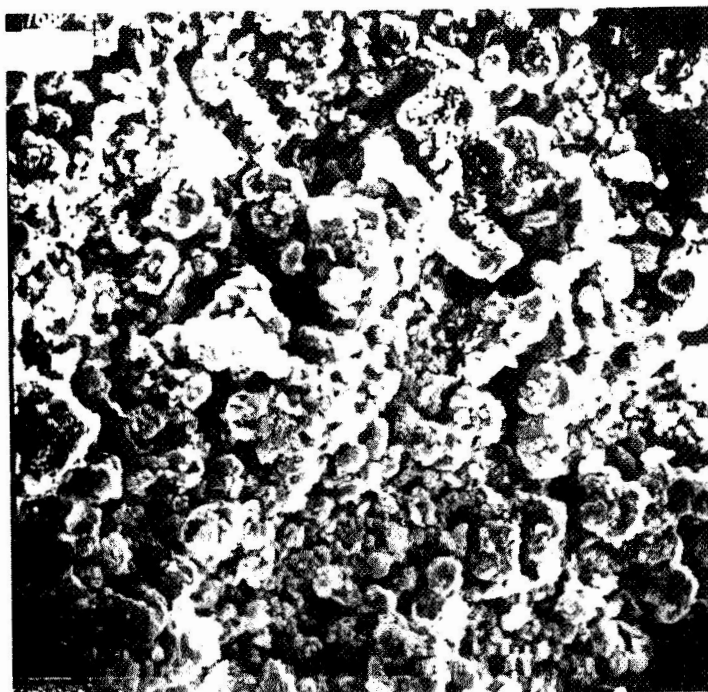


Figure 69. SEM OF ZrO₂-D (1,000X)

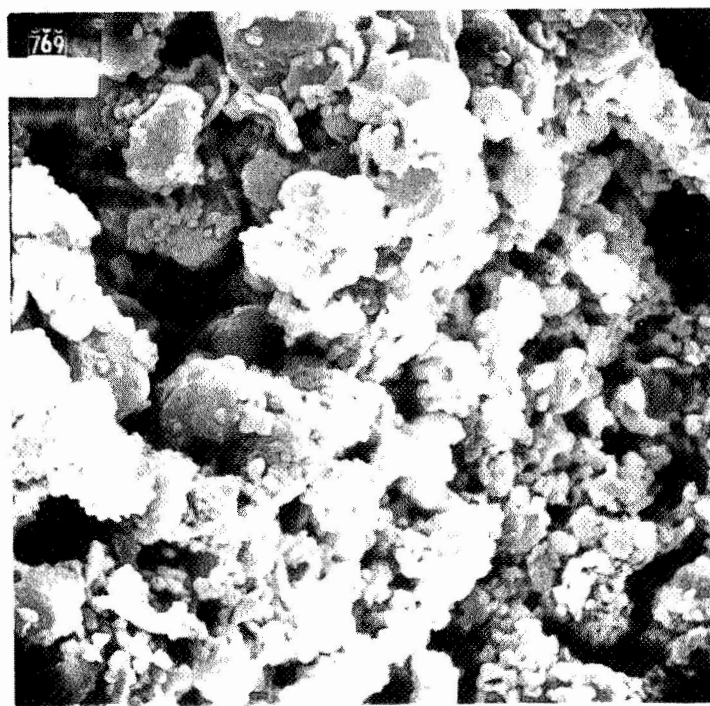


Figure 70. SEM OF ZrO₂-D (3,000X)

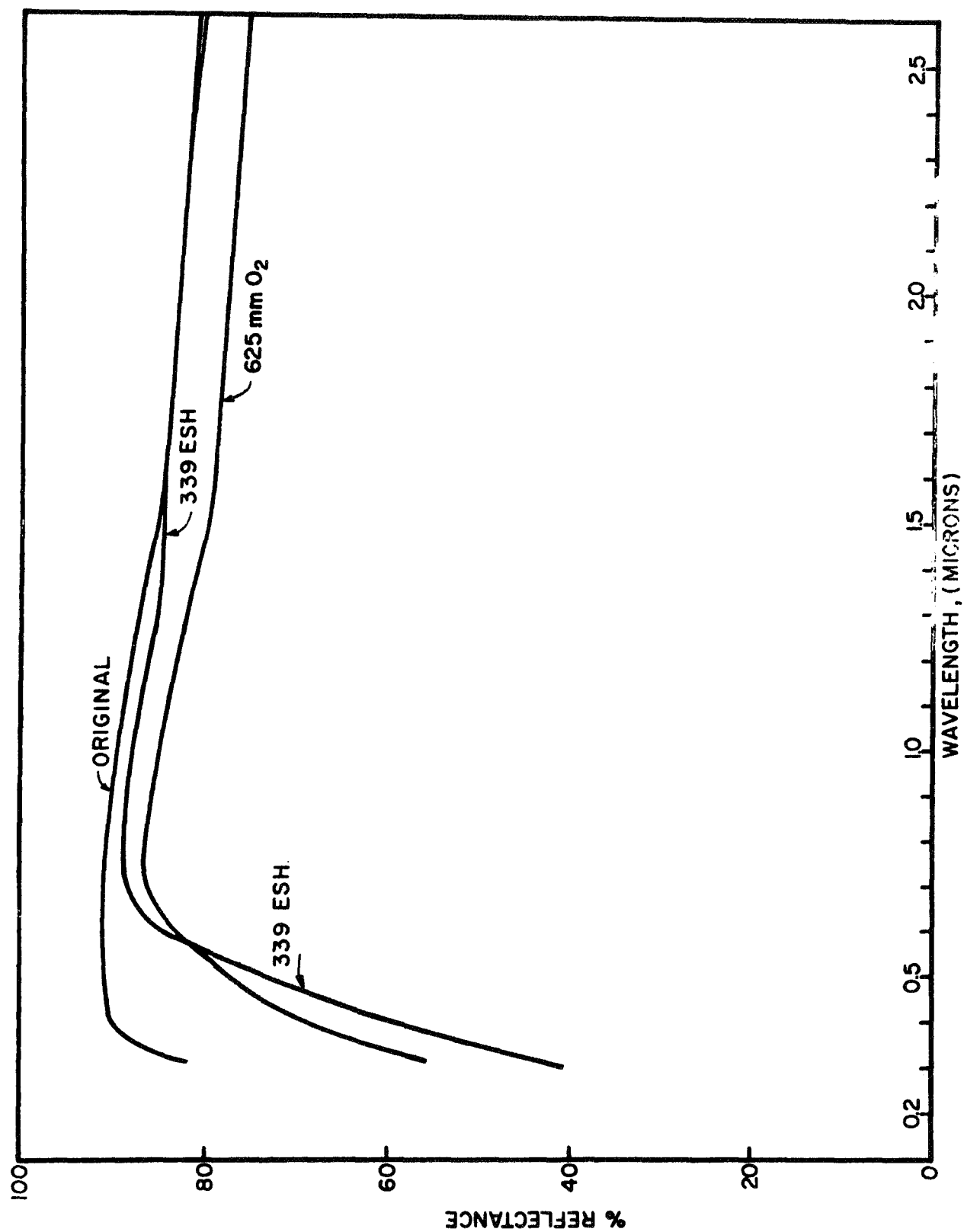


Figure 71. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS LINDE A - DISPERSED

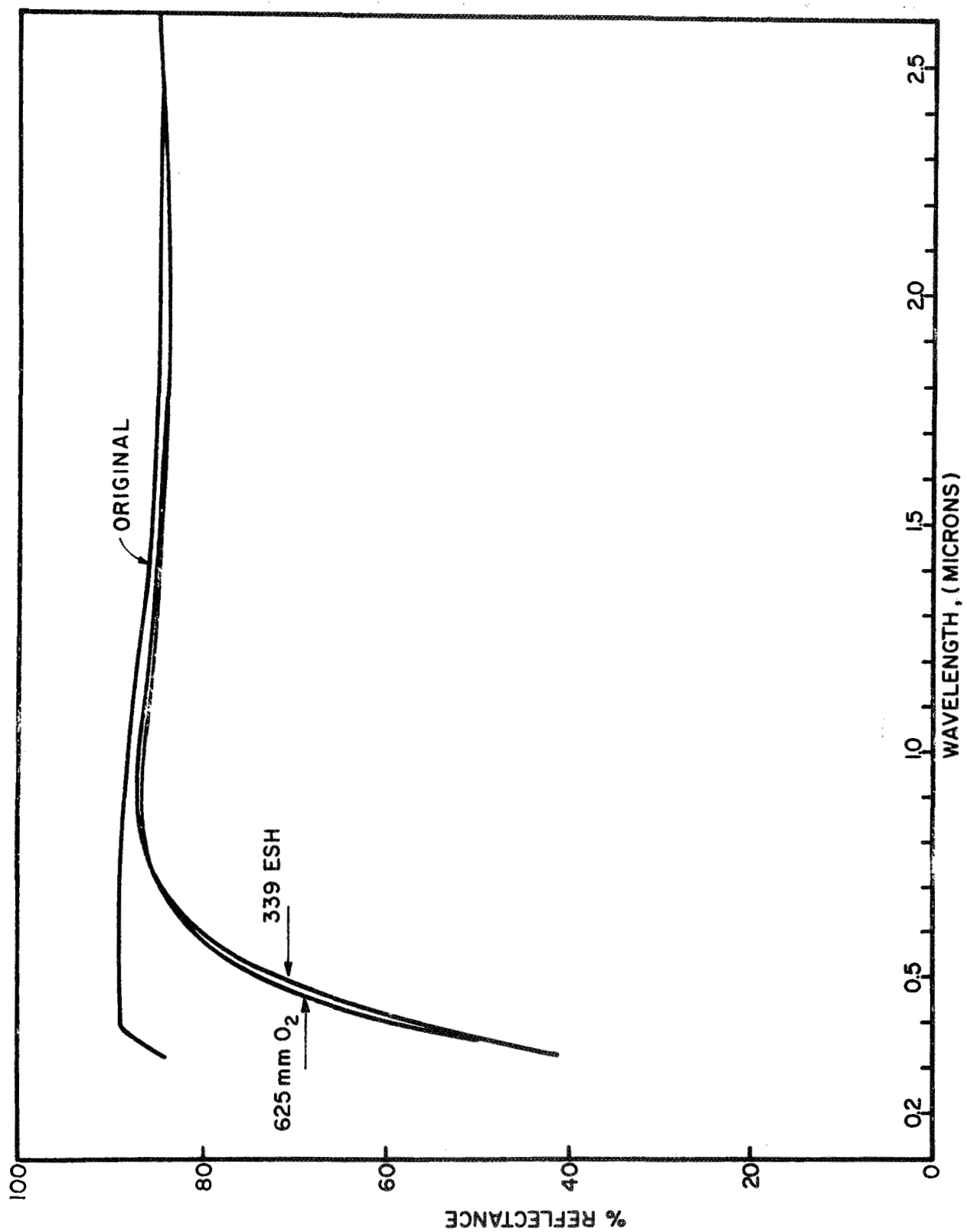


Figure 72. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS LINDE C - DISPERSED

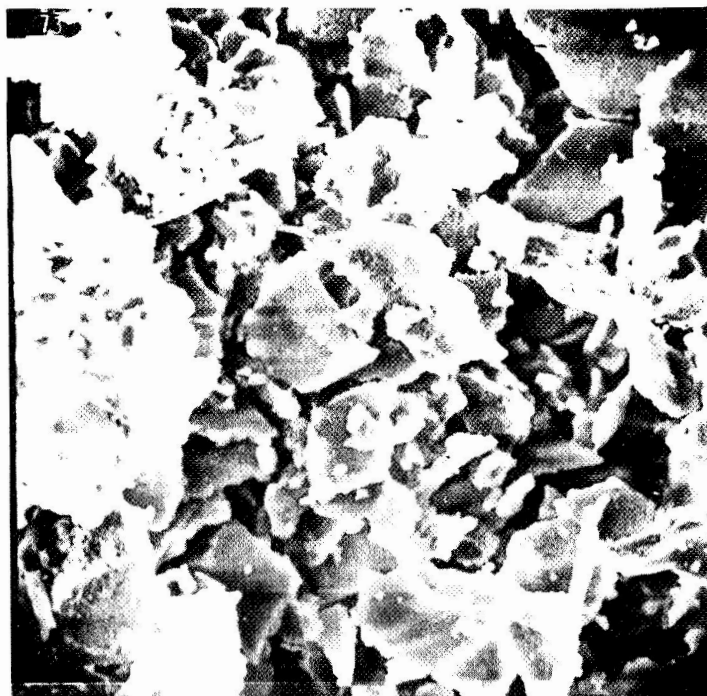


Figure 73. SEM OF LINDE C-U BINDERLESS (300X)

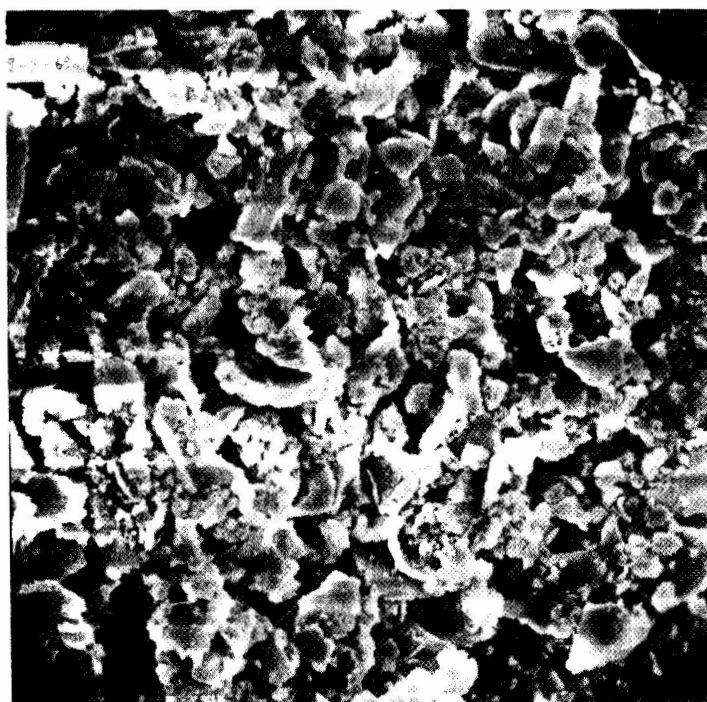


Figure 74. SEM OF LINDE C-D BINDERLESS (300X)

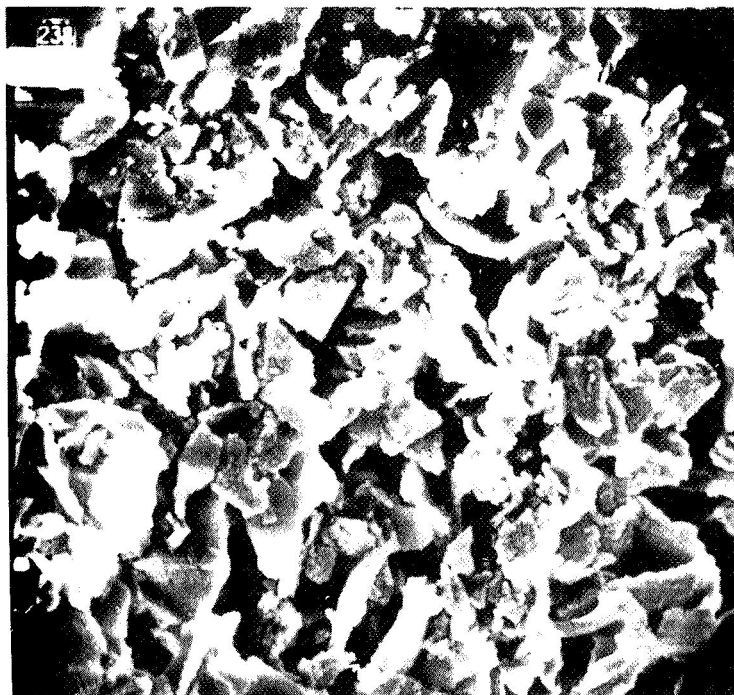


Figure 75. SEM OF LINDE A-U BINDERLESS (300X)

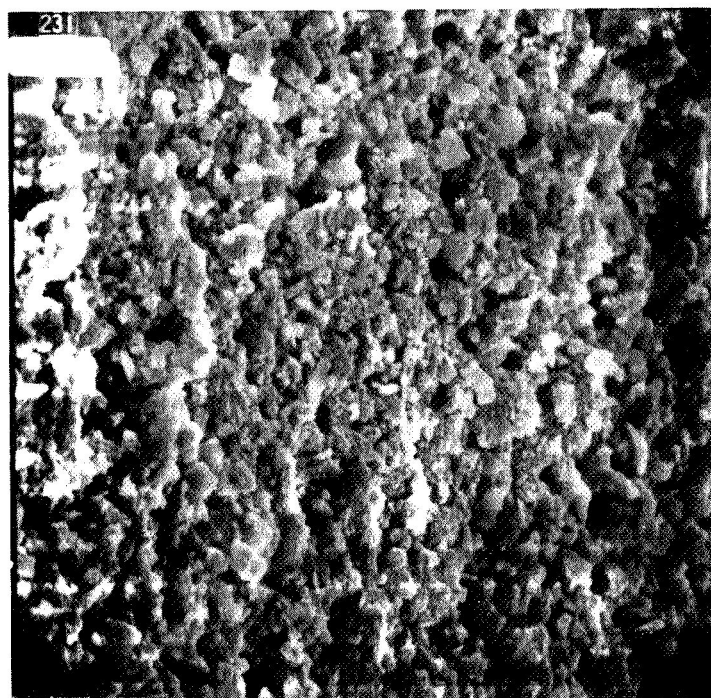


Figure 76. SEM OF LINDE A-D BINDERLESS (300X)

films are at first glance more dramatic than their optical differences, yet there are subtle differences which have optical significance. The void structure, for example, always correlates with high reflectance. The fact that discrete particle sizes are not altered by dispersion and that they are very nearly the same for Linde A and Linde C explains why the ultraviolet induced damage in Linde A and Linde C appear very similar. The damage occurs mainly in the ultraviolet region of the spectrum where discrete particle size is most likely the dominant factor.

The remaining spectra and SEM pix are of Meller pigments. The binderless films of these materials apparently rely upon moisture for their cohesiveness, and in the IRIF some of them flaked rather badly. The films of dispersed materials exhibited better cohesion and adhesion than did those prepared from undispersed powders. We can compare on a relative basis the original and damage spectra in films of dispersed and undispersed powders as well as their SEM pix. Figure 77 shows M-0.3-D (Meller's 0.3 μ -dispersed), and Figures 78 and 79 are the SEM pix of the films prepared from undispersed and dispersed powders, respectively.

In Figures 80 and 81 are the spectral-reflectance curves for M-1.0-U and M-1.0-D, respectively. The SEM pix for M-1.0-U are in Figures 82, 83 and 84; for M-1.0-D, in Figures 85, 86 and 87. Again, the action of dispersion in removing voids is obvious; the average aggregates sizes are smaller because of dispersion and the debris of broken aggregates fill up the void spaces. Note, also, in Figures 84 and 87 that the discrete particle size remains unaltered by dispersion and that there are voids, not only between aggregates, but in the aggregates.

Similar remarks can be made about M-3.0-U and M-3.0-D whose spectral reflectance spectra appears in Figures 88 and 89 respectively. Representative SEM pix for M-3.0-U are in Figures 90 and 91 and for M-3.0-D in Figures 92 and 93. The most interesting feature of the reflectance spectra is the amount of relative

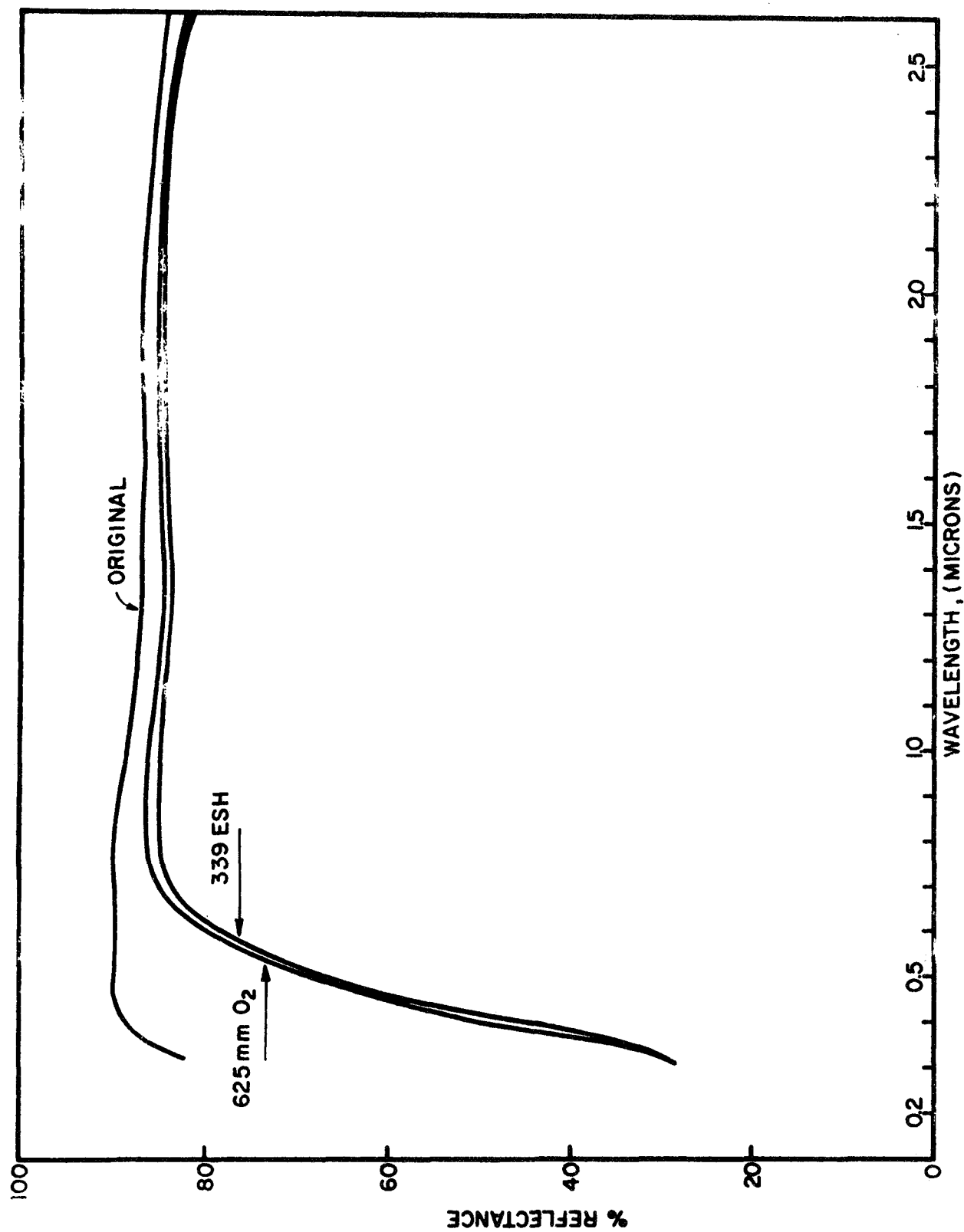


Figure 77. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS
MELLER 0.3 μ - DISPERSED

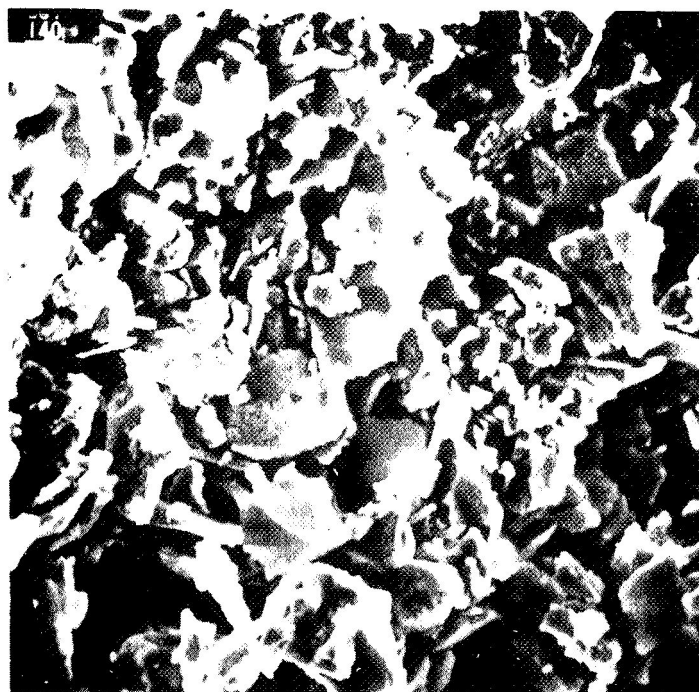


Figure 78. SEM OF M-0.3-U BINDERLESS (300X)

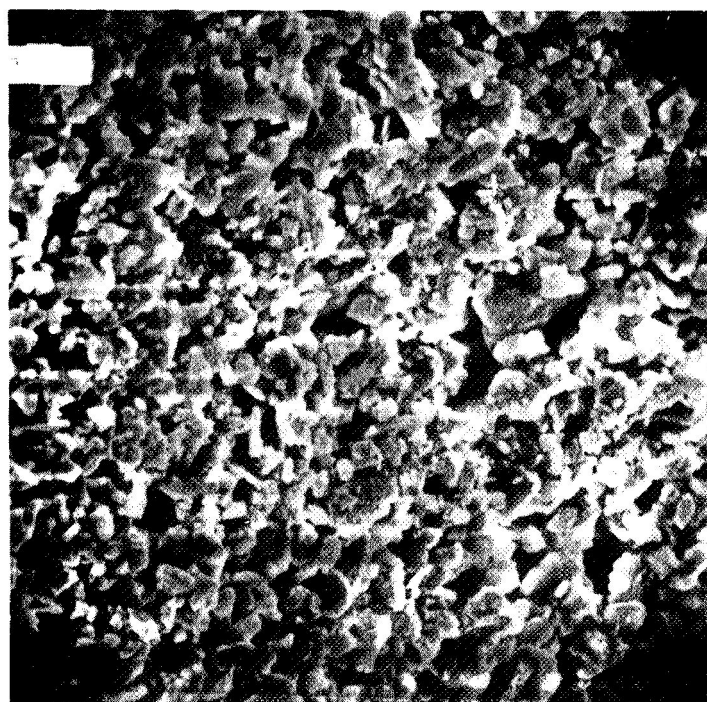


Figure 79. SEM OF M-0.3-D BINDERLESS (300X)

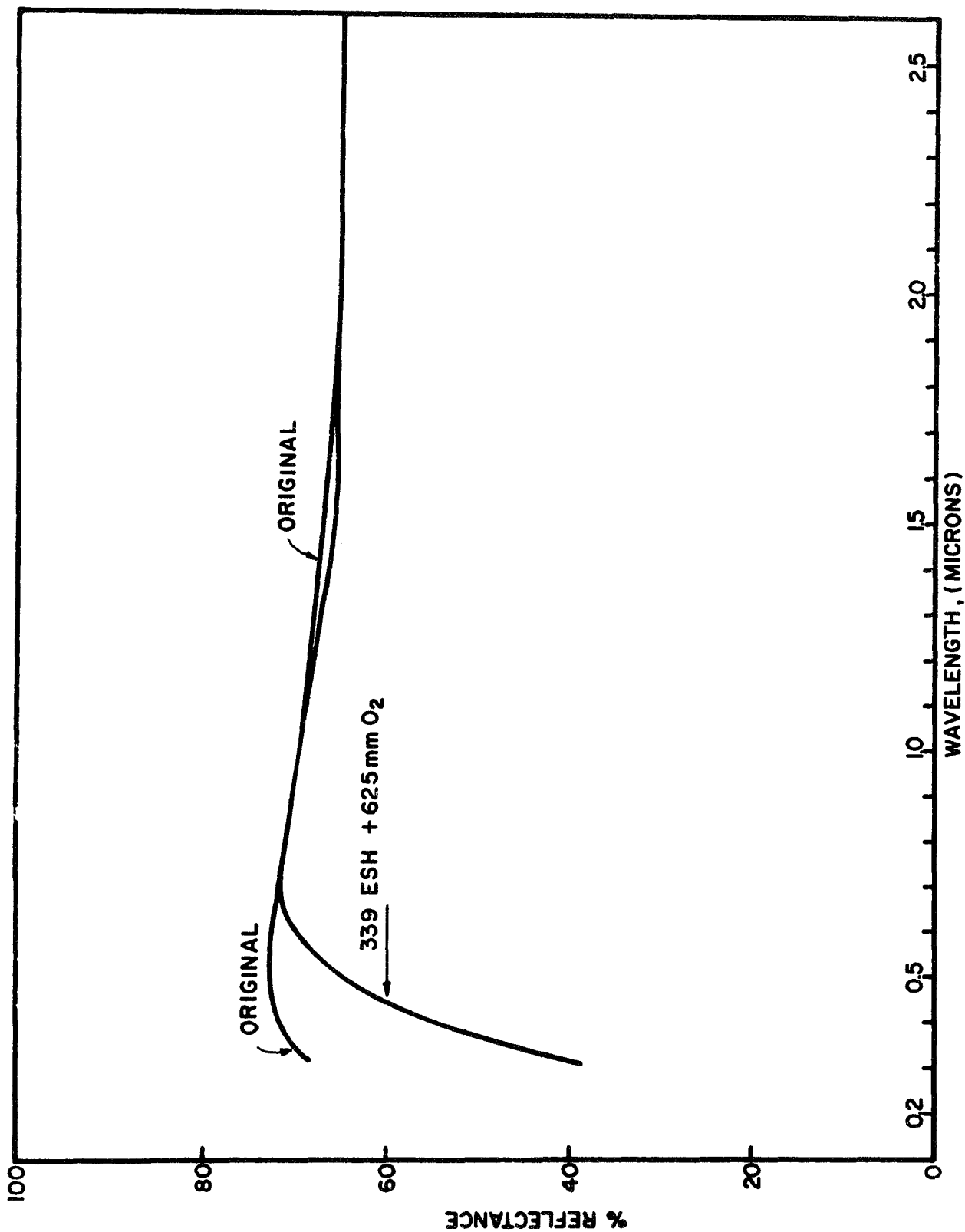


Figure 80. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS MELLER 1.0 μ - UNDISPERSED

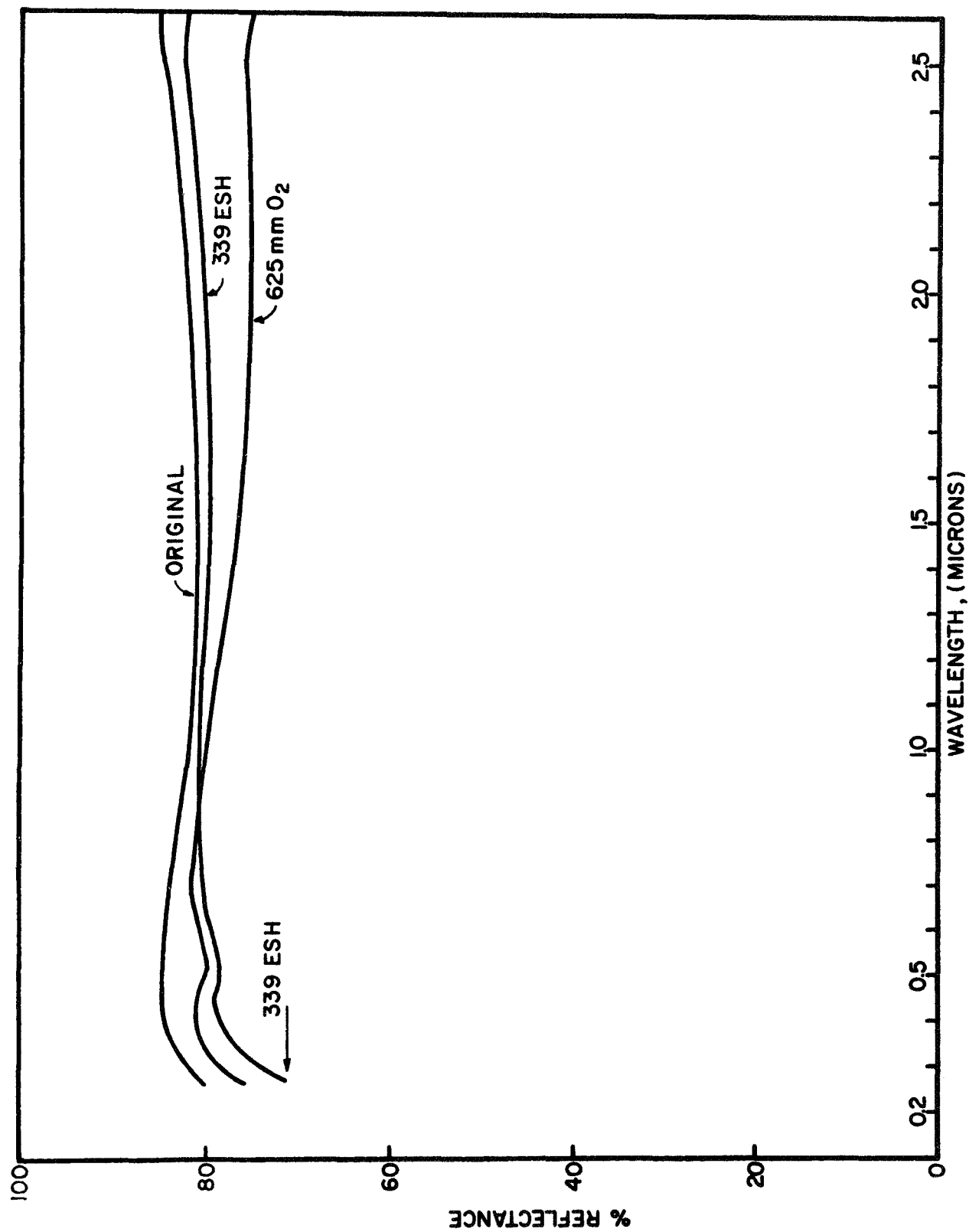


Figure 81. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS MELLER 1.0 μ - DISPERSED

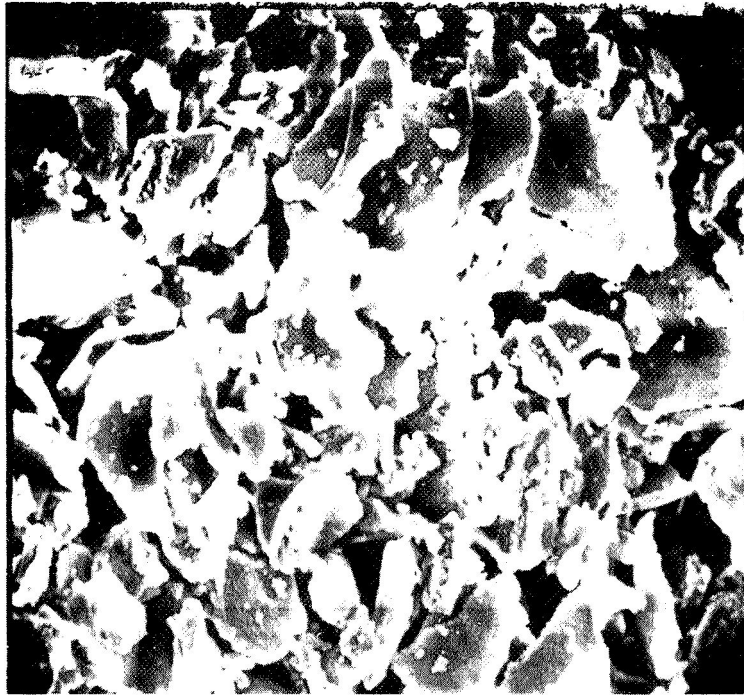


Figure 82. SEM OF M-1.0-U BINDERLESS (300X)

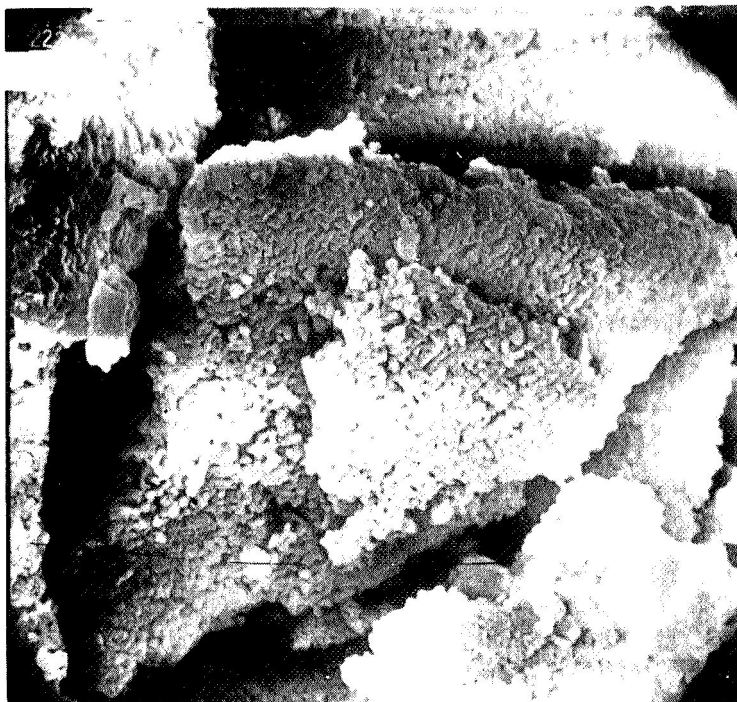


Figure 83. SEM OF M-1.0-D BINDERLESS (3,000X)

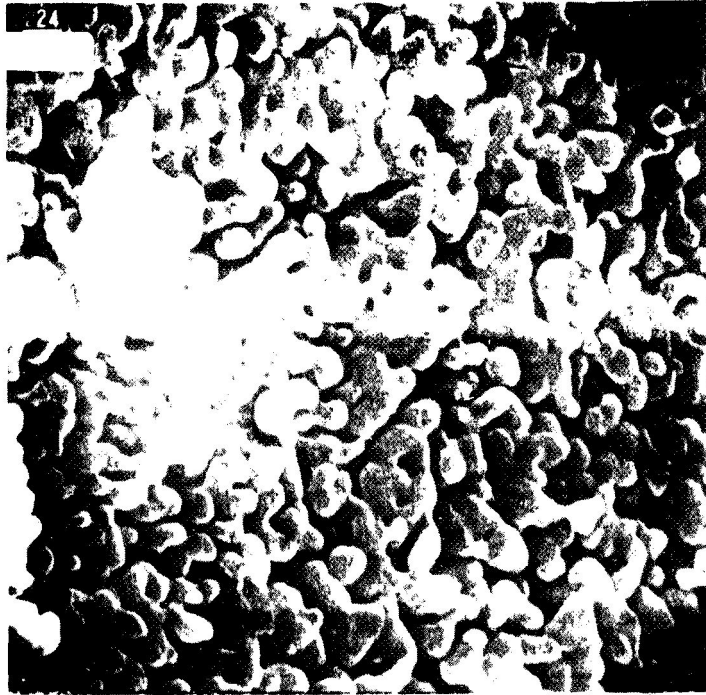


Figure 84. SEM OF M-1.0-U BINDERLESS (10,000)

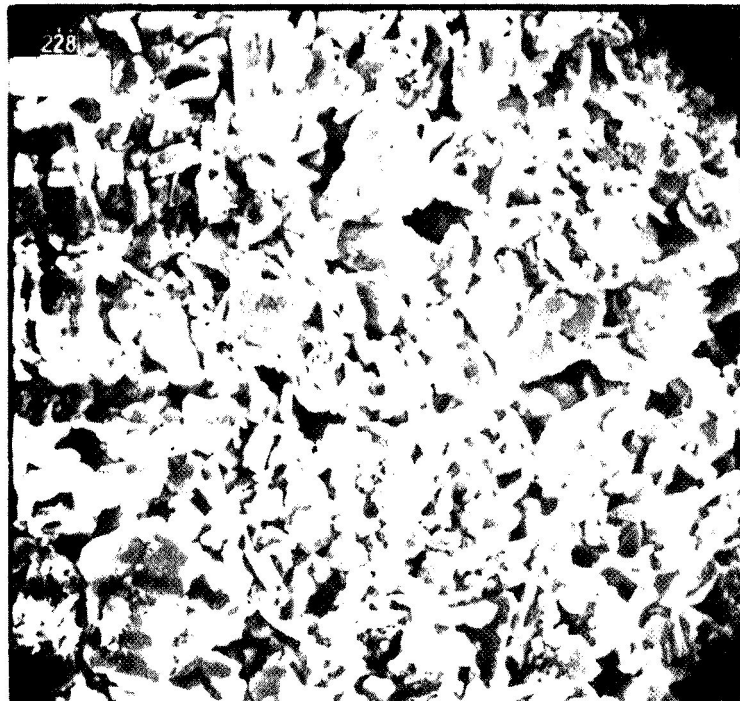


Figure 85. SEM OF M-1.0-D BINDERLESS (300X)



Figure 86. SEM OF M-1.0-D BINDERLESS (3,000X)

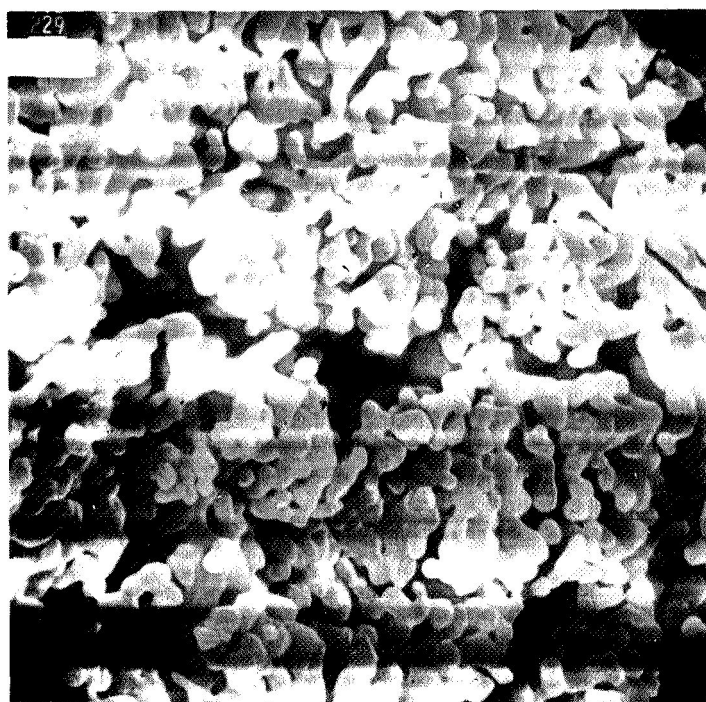


Figure 87. SEM OF M-1.0-D BINDERLESS (10,000X)

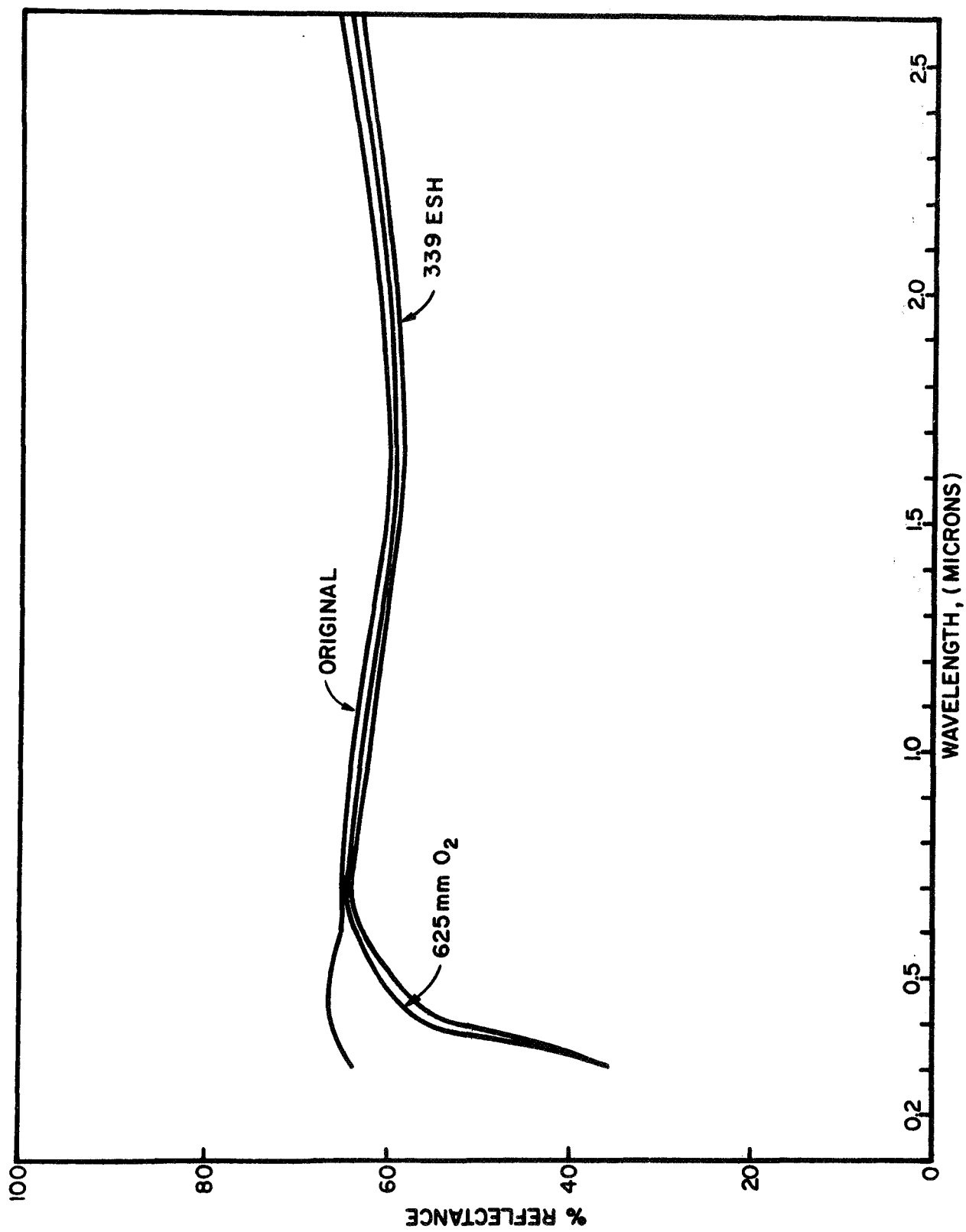


Figure 88. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS MULLER 3.0 μ - UNDISPERSED

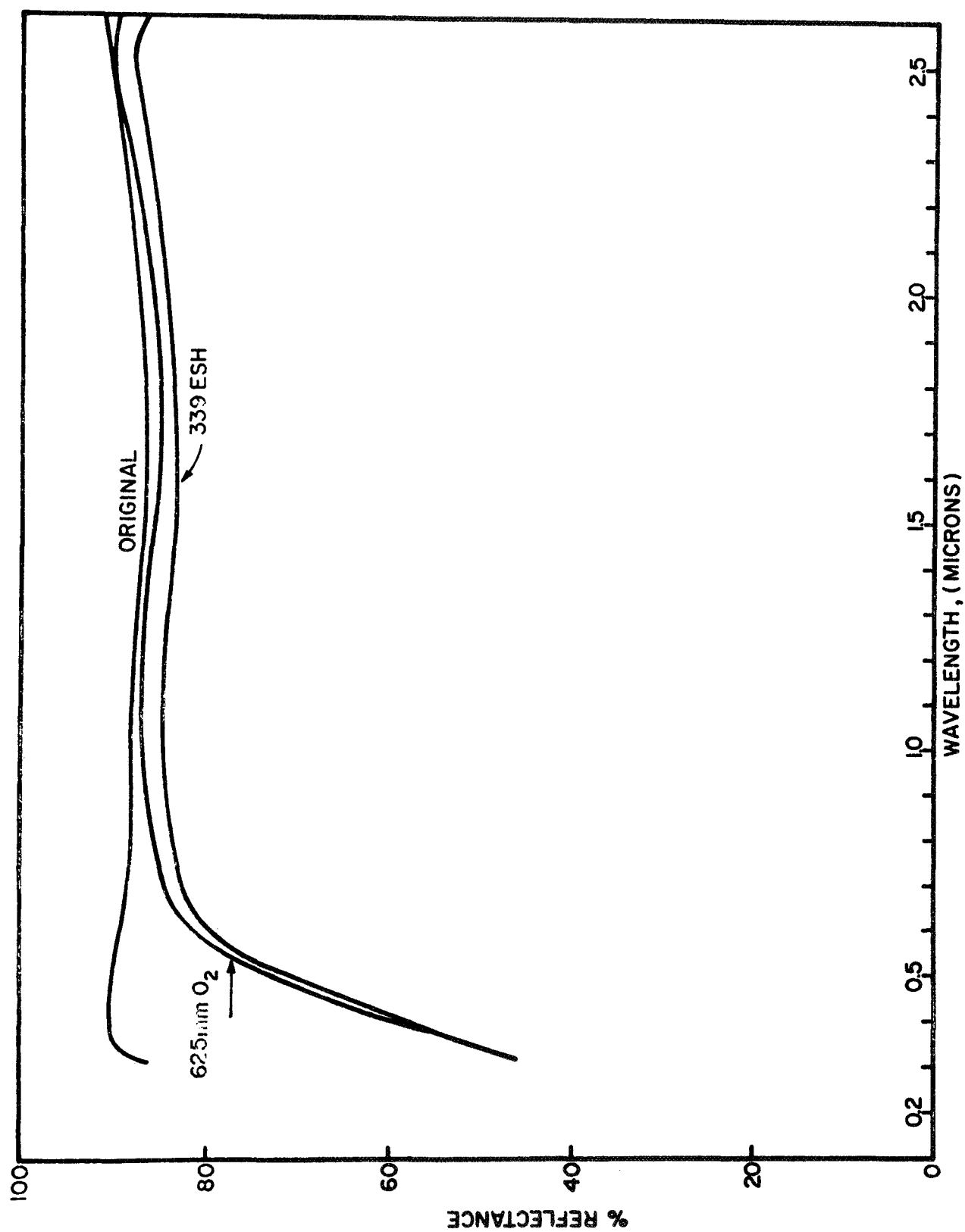


Figure 89. EFFECT OF 339 ESH ULTRAVIOLET IRRADIATION ON BINDERLESS MELLER 3.0μ - DISPERSED

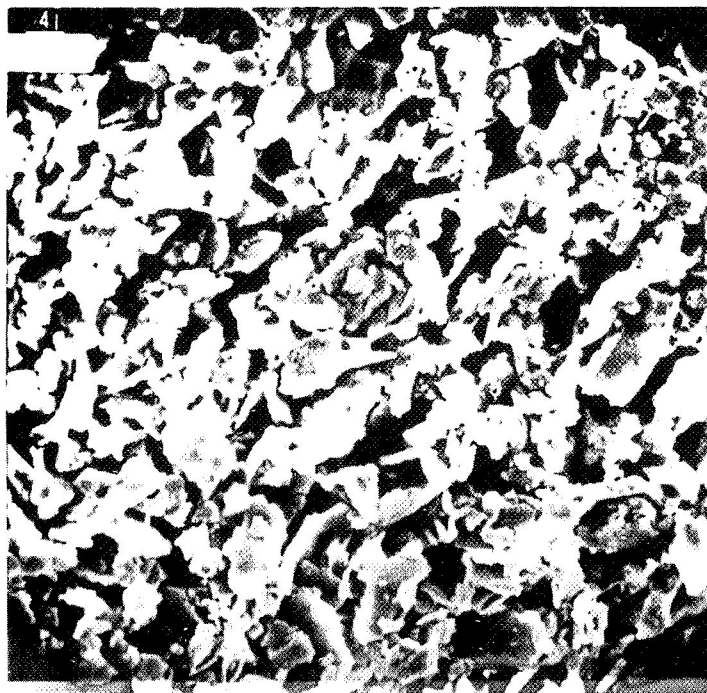


Figure 90. SEM OF M-3.0-U BINDERLESS (300X)



Figure 91. SEM OF M-3.0-U BINDERLESS (3,000)

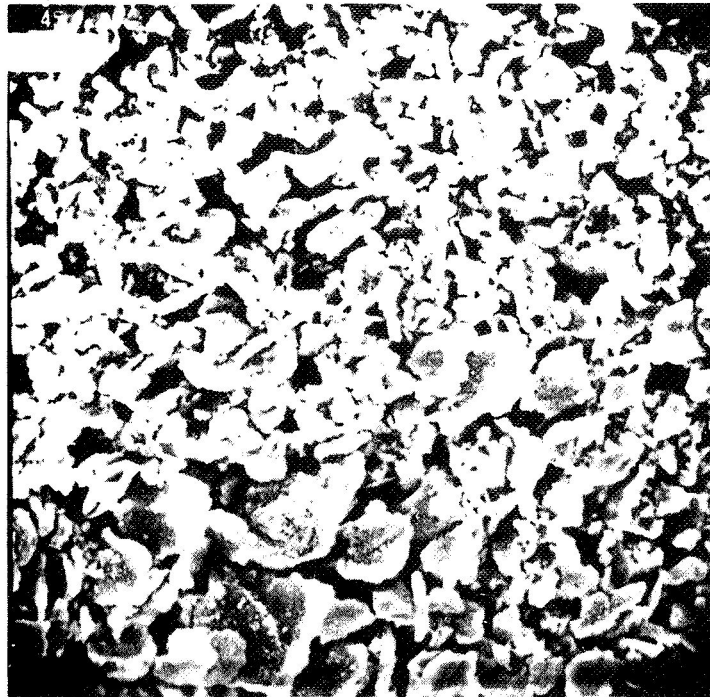


Figure 92. SEM OF M-3.0-D BINDERLESS (300X)

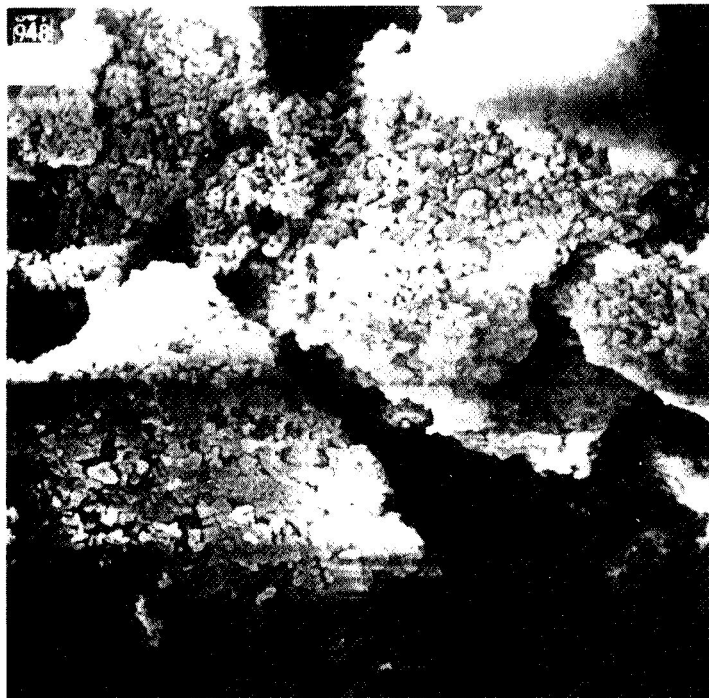


Figure 93. SEM OF M-3.0-D BINDERLESS (3,000X)

spectral reflectance damage between 0.3 and 0.7 μ . All of the dispersed pigments display extensive damage in this region; the undispersed pigments do not. The M-1.0-D spectra are an apparent exception; the M-1.0-D coating, however, flaked badly during irradiation and the validity of its post-test spectra is questionable. Nevertheless, the SEM pix bear out the differences which dispersion makes in film structure, and the spectral reflectance curves and the reflectance degradation spectra reveal a relationship to film structure.

The question then of what effect particle size has on damage spectra becomes essentially the same question as that of what effect does it have on spectral reflectance. The film structure, the physical and geometrical relationships existing between particles, voids and aggregates, almost entirely determines the spectral reflectance characteristics. In the above examples, dispersion apparently increases the ultraviolet damage effect. This, we think, is because the void structure between aggregates is reduced and, as we observed earlier, voids tend to mitigate the absorption effect, and consequently the lesser the void density, the greater is the net absorption effect.

VII. CONCLUSIONS

There are different categories of conclusions that have been reached; some pertain to light scattering theory, some to experimental procedures and techniques and still others to materials behavior.

With respect to light scattering, we have formed the following conclusions:

Light scattering in dense dielectric powders cannot be treated accurately either by Mie Theory or by Monte Carlo applications of Mie Theory, because in this case neighboring particles have more than a simple geometric influence upon one another.

The reflectance of a paint film can be expressed in a functional relationship, as

$$R_{\lambda} = R_o \left[\sum_i \Delta k_i, t, \frac{n_p}{n_v}, \sum_i k_{i,o}, d_v, d_p, d_A, \text{PVC}, \lambda \right] \quad (56)$$

If the percentage change in R_{λ} for a given fractional change in one of the bracketed parameters is a measure of the sensitivity of that parameter, then we suspect that the order of sensitivity of each parameter--from the most to the least sensitive--is that given. Note that Δk_i is the environment-induced absorption, while $k_{i,o}$ is the natural or impurity absorption.

If materials' parameters and original paint film thickness are fixed, then, as the above expression shows, the reflectance is mainly dependent upon the geometrical structure of the paint components; that is, upon the sizes and shapes of discrete particles and aggregates and upon the spaces between them, whether they are void or filled with a binder.

Scattering by pigmentary particles intensifies the net absorption effect. Hence, the wavelength of maximum particle scattering should not be allowed to be in the spectral region of induced damage. As a general rule, materials which degrade principally in the infrared should be optimized for high visible reflectance; those which degrade in the visible and near ultraviolet should be optimized for high reflectance in the long wavelength visible and near infrared region. Ultraviolet reflectance should not be maximized in dielectric materials (e.g., Al_2O_3 , SiO_2) because of very high intrinsic absorption in the far ultraviolet and significantly high impurity and induced absorption in the near ultraviolet.

The contribution of voids to the total spectral reflectance is a major one because they increase spectral reflectance and tend to mitigate the absorption effect of intrinsic absorbers. Voids may occur either between pigment particles or in the binder (air occlusions, for example) and techniques can be developed to maximize their effect.

Certain of the data clearly indicate that pigmentary scattering intensifies absorption while void scattering tends to decrease it. There are, however, a few data which indicate oppositely. While this dilemma has not as yet been resolved, it is abundantly clear that scattering does modify theoretical considerations based on a purely physical approach. Compare, for example, the case of two identical spherical particles both of a diameter, d_p , and separated by a distance, say, $10 d_p$ between centers, with the case where these particles are touching or nearly touching. To an incident beam of light, is the latter system of two particles equivalent to the first? We suspect

not, on the grounds that in the latter case, the surface forces of the particles are interacting and the electromagnetic fields of each are modified by the presence of the other. The presence of surface forces and their fields which extend beyond the physical dimensions of a particle become greater with decreasing particle size. The field surrounding an isolated spherical particle should be symmetric, but it will almost certainly be greatly altered by the proximity of a similar particle. The absorption effect also would be expected to be very substantially affected.

The reflectance of a binderless paint film exceeds that of a pigment-binder system not just because of a higher $m = (n_p/n_v)$ ratio, but also because of the closer packing and better pigment structures attainable in the binderless system.

The broad region of high spectral reflectance in dielectric powders results from the respective contributions of particle, void and aggregate scattering. In a relative sense the reflectance at the shortest wavelengths results mainly from voids (if any) within discrete particles (e.g., from the holes in donut shaped particles); at progressively longer wavelengths it results from discrete particle size, voids between particles, voids between aggregates, and at the longest wavelengths, from aggregates.

Regarding the experimental procedures and techniques we can say the following:

Binderless films are much more easy to prepare and characterize than pigment-binder systems, especially with respect to geometric structure.

The SEM technique for particle and film geometries and structures is a very powerful and useful one,

provided that reflectance spectra are taken on identical films. Great care must be taken to insure equivalence. The fluff factor (inverse film density) can be varied over a significant range of values. But, since it has been nearly impossible to reproduce a given fluff factor - even under the most exactly reproduced conditions and carefully controlled procedures - a statistical approach is required to separate void volume effects from mass and thickness effects. (The fluff factor is related to the film thickness/film mass ratio.)

The most reproducible and consistent binderless films are obtained by methods which depend very strongly on the material, its particle size and shape characterization; and upon the state of aggregation. For each material there is an optimum method. In other words, the methods for obtaining consistent and reproducible films of binderless materials is essentially unique for each material.

The process of spraying pigment-binder systems will inevitably incorporate air (or, spray propellant) "voids" in the films, increasing the reflectance. Consequently, care must be exercised to prevent air (or gas) entrapment in the cured film, if the properties of the film itself are the main interest.

The basic data needed to characterize a binderless film are the reflectance spectra, mass/unit area of coating, average thickness of coating, the paint components, SEM photomicrographs at various magnifications, and particle size and shape distributions.

Materials behavior is a fascinating problem area. Some of the more important observations and conclusions are:

We believe that the reflectance of binderless paint films is a sensitive function of preparation

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techniques. From the difficulties we have had in reproducing films, it is obvious that much more care in preparation and characterization must be taken in support of comparative tests and evaluations. The random results obtained in previous round robin tests may be attributable in large part to subtle, yet random, differences in the samples.

The size and shape distributions of a system of finely divided particles determines the structure of a binderless film. The vehicle, the rate of deposition and the PVC of the initial spray solution also affect the film structure. The more volatile the vehicle is and the slower the deposition rate, the more fluffy the resulting film.

The most dense of the binderless films usually were those whose particle size distributions were broad. The increased density results from the small aggregates and fragments of aggregates filling spaces which otherwise would have been voids. While it thus might appear that narrow distributions would result in the more fluffy coatings, there are two additional considerations which make this assertion rather tenuous. First, the distributions of sizes and shapes of discrete particles directly influences the distribution of sizes and shapes of the agglomerates which form from them and, evidently, the rates at which they form. Second, discrete particles and agglomerates will always be present, but their relative amounts will vary considerably according to preparation parameters. For high broad band reflectance, a range of effective particle sizes, from single (discrete) up to large agglomerates, is needed.

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